

Research Article

Enhancement of Fischer-Tropsch Synthesis by Periodical Draining of the Wax-Filled Pores of a Cobalt Catalyst by Hydrogenolysis

Carsten Unglaub, Johannes Thiessen, Andreas Jess *

University of Bayreuth, Chair of Chemical Engineering, Center of Energy Technology
Universitaetsstrasse 30, 95447 Bayreuth, Germany; E-Mails: carsten.unglaub@uni-bayreuth.de;
johannes.thiessen@uni-bayreuth.de; andreas.jess@uni-bayreuth.de

* **Correspondence:** Andreas Jess; E-Mail: andreas.jess@uni-bayreuth.de

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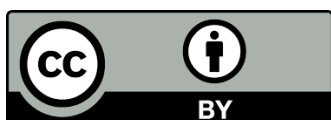
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Abstract

Fischer-Tropsch reactors operated in a steady state suffer from a low pore effectiveness factor and a high methane selectivity caused by internal mass transfer limitations due to the accumulation of long-chain hydrocarbons inside the catalyst pores. Therefore, an alternating process switching between Fischer-Tropsch synthesis (FTS) and drainage of the pores by hydrogenolysis is proposed. The periodical cracking of the accumulated waxes within the (partially) filled pores, realized by a switch from syngas (H_2 , CO) to pure hydrogen, results in a higher overall catalyst productivity and a more favorable product distribution. The influence of temperature and time of FTS on drainage time and product distribution was experimentally investigated at typical temperatures of FT fixed bed processes in a range of 210 to 240°C. Alternating drainage of the pores by hydrogenolysis at a hydrogen partial pressure of just 1 bar leads to an improvement of the rate of CO conversion by up to 90% (240°C, 2 h FTS) and an improvement of even 120% concerning the rate of production of non-methane hydrocarbons (240°C, 2 h FTS).



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Keywords

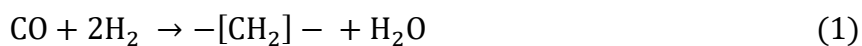
Hydrogenolysis; energy storage; pore draining; Fischer-tropsch synthesis

1. Introduction

In order to reduce greenhouse gas emissions, the capacities of renewable electricity production are steadily increasing. But, electrical energy from renewable sources like wind or solar is seasonal and fluctuates. Hence, cheap and efficient storage techniques must cope with the gap between renewable energy supply and power demand. Several techniques of direct electrical energy storage, like batteries and capacitors or indirect storage by thermal masses or hydrogen, are currently examined. But, most storage strategies suffer from low gravimetric and/or volumetric energy density, high costs, or high conversion losses in the case of liquefied or adsorbed hydrogen [1, 2]. Overall efficiency is reduced by adding new transformation processes, and therefore chemical energy storage is mostly only reasonable if needed. For applications like jet fuel or marine diesel oil, which require high energy density and easy long-term storage, chemical conversion of (renewable) H₂ with carbon oxides (CO, CO₂) to liquid fuels like methanol or alkanes by Fischer-Tropsch synthesis (FTS) becomes feasible. Alkanes benefit from a very high energy density (e.g., diesel oil 36 GJ m⁻³), justifying the additional energy needed for conversion [3-5]. In addition, long-distance transportation by ship or air based on battery electric, hydrogen, or hydrogen fuel cell-driven systems is today still not viable.

The concept of chemical energy storage using carbon capture and conversion (CCC) comprises generation of syngas (H₂ and CO_x): Renewable H₂ can be produced by water electrolysis based on renewable electricity. For FTS, CO and not CO₂ are needed to produce liquid fuels like jet fuel and chemicals ranging from short-chain olefins to lubricants [6-8]. So, CO₂ has to be converted to CO by the reverse water-gas shift reaction to provide the syngas optimal for FTS. (Remark: There is ongoing research on CO₂-based FTS, see, e.g. [9], but until now, industrial FT processes still rely on CO-based syngas.)

FTS can generally be grouped into two operation modes. The low-temperature process (LTFT, 200-240°C), which employs mainly cobalt catalysts, has a high selectivity to linear high molecular paraffin; the high-temperature (HTFT, 300-350°C) process based on Fe-catalysts produces mainly gasoline and short-chain olefins. In this paper, only LTFT with Co as a catalyst is considered and discussed. Long-chain paraffin obtained from LTFT has to be processed further to diesel and jet fuel by mild hydrocracking to achieve an overall fuel selectivity of up to 80% [4, 10]. Since hydrocarbon chains are formed by successive incorporation of carbon units and hydrogen into a hydrocarbon chain, the FTS can be regarded as a solid-catalyzed polymerization reaction represented by [11]:



As in many polymerization reactions, the product distribution is governed by the Schulz-Flory distribution using the probability of chain growth α (Eq. (2)). The value of α depends on the reactant concentration(s), catalyst, and temperature, whereby already small variations of the value of α cause a severe shift of the product selectivity and distribution [11, 12].

$$w_n = n_n(1 - \alpha)^2 \alpha^{n-1} \quad (2)$$

During the initial phase of low-temperature FTS at typical industrial process conditions and particle diameters in a range of mm, used for fixed bed synthesis, long-chain hydrocarbons (HCs) will condense in the pores of the particles and finally fill the porous system of the catalyst. The initial period of accumulation of these waxes, which typically lasts a day, can cause severe problems and drawbacks. First, the complete filling of the pores by liquid HCs leads to severe internal mass transport resistances ($D_{gas} \approx 100 D_{liq}$), resulting in a lower overall effective activity [13]. Second, the H_2/CO ratio increases towards the center of the catalyst, which can result in a higher methane selectivity and lower chain growth probability. Right at the beginning of the reaction, when no wax is inside the catalyst pores, the FTS is seen as a gas-solid reaction. While proceeding, wax accumulates inside the catalyst, and the characteristic of the reaction shifts to a three-phase reaction (gas, solid, liquid). As soon as the first layer of wax is deposited, a vapor-liquid equilibrium has to be considered for calculating prevailing reactant concentrations. According to the Henry coefficients, CO solubility is higher than the hydrogen solubility in typical FTS products [14]. But, hydrogen diffusion is much faster than the diffusion of carbon monoxide through the wax. Thus, CO depletes towards the catalyst core, and the H_2/CO -ratio increases, and thus the chain growth probability decreases, leading to unfavorable product selectivity. The diffusion length increases with the increasing pore filling degree since the wax layer thickness increases, and it grows substantially when transportation pores (macro pores) fill [12, 15-19]. For high productivity regarding fuels like kerosene or diesel, a chain growth probability of at least 0.85 is needed and should be obtained at any time (cobalt, LTFT) [19]. In general, the accumulation of liquid HCs (wax) inside the pores of the catalyst is considered harmful to both catalyst activity and process selectivity. However it has to be accepted for steady-state FT processes. Catalyst lifetime, activity, and product selectivity are also important for the viability of an efficient FT process and are, therefore, also of interest for investigation and optimization [20].

Reactivating the catalyst by repetitive removal of accumulated wax is not a new idea. In the early 1940s, Otto Roelen at Ruhrchemie reported a successful reactivation procedure of a deactivated cobalt catalyst by hydrogenation of the hydrocarbon deposits at around 200°C and at 0.75 bar hydrogen pressure [21]. But, this approach was not pursued further since better heat management and modern reactor design promised more improvement. In the recent past, it has been tried to decrease the pore diffusion resistance by in situ extraction of wax using supercritical or near-critical solvents, which however, comes with the drawback of the need for an additional solvent and high process pressure [22-24].

Hydrogenolysis (HGL) is characterized, at least concerning alkanes, as the break of C-C bonds in the presence of hydrogen, leading to alkanes of lower molar mass by eliminating short chain alkanes, mainly methane. Since hydrogenolysis is often referred to as parasitic and unwanted, most publications focus on how to avoid or minimize it [25]. The first step is the dissociative adsorption of hydrogen, and the initial break of C-H bonds before the C-C bond rupture of the alkane backbone occurs on the catalyst surface and subsequently, carbon-hydrogen bonds reform. The degradation of alkanes can be described by the Kempling – Anderson scheme depicted in Figure 1. This reaction scheme consists of a combination of two processes: 1) predominantly but not exclusively cracking of primarily the terminal C-C bond, which produces mainly methane, and 2) the desorption of the

remaining alkane rest. Thus, the product selectivity depends on the ratio of cracking rate (k_i) and rate of adsorption and desorption (k_i^+ , k_i^-). The alkane is cracked as long as the remaining alkane stays adsorbed. Thus, high methane selectivity results from fast alkane cracking or slow desorption. The desorption rate is low in case of high conversion and, thereby high alkane partial pressure in the gas phase or the low vapor pressure of particularly long-chain hydrocarbons [25, 26].

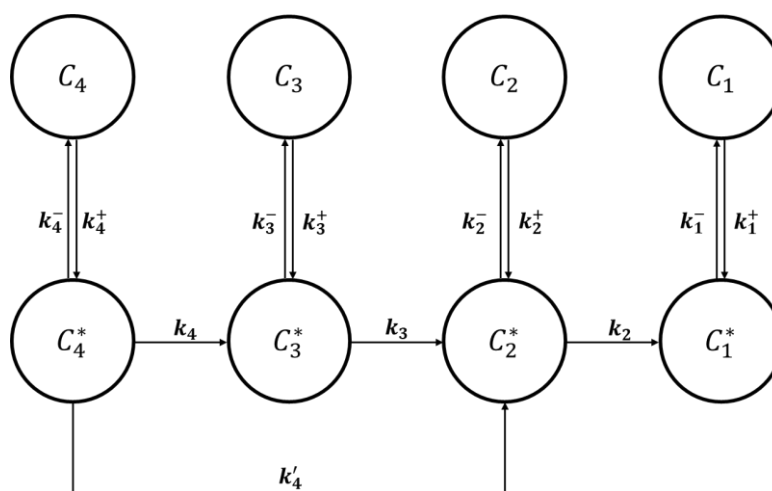


Figure 1 Hydrogenolysis of butane according to a reaction scheme proposed by Kempling and Anderson [26].

The rate of hydrogenolysis can be correlated with reactant pressure by the following power rate law [27]:

$$r_{HGL} = k P_{alkane}^n P_{H_2}^m \quad (3)$$

where n is positive and often regarded as one or close to one. On the other hand, m is not constant and depends highly on the temperature, pressure, and chain length of the reactant. At very low hydrogen pressures, the reaction order is $m > 0$ until a maximum reaction rate is reached. Then the reaction becomes more and more hindered by hydrogen, and the reaction order, therefore, turns negative ($m < 0$). Frequently, a strong negative reaction order in a range of -2 to -3 is reported. In general, m increases with increasing temperature because at a higher temperature, less hydrogen is adsorbed on the catalyst surface resulting in less hindrance of the initial C-H bond rupture [28-30].

Long-chain alkanes have a more attractive interaction with the catalyst, which facilitates the activation of dehydrogenation and stabilizes the transition state. Thus, the overall reaction rate of hydrogenolysis increases with alkane chain length, and the maximum rate shifts to higher hydrogen pressures [29, 31, 32].

The process outlined in this publication consists of an alternation between FTS and hydrogenolysis in order to reduce the number of long-chain hydrocarbon deposits in the catalyst pores (filling degree of pore system), leading to improved activity and product selectivity. Based on the preliminary work by Duerksen et al. [33], an attempt was made to improve and optimize the process even further by increasing the content of cobalt to a value more typical for industrial operation (20 wt.-% Co instead of 10%) and applying more ambitious reaction conditions (higher reaction temperature and lower hydrogen pressure during hydrogenolysis) [34]. Furthermore, an

overview of wax accumulation during FTS inside the porous catalyst over a broad temperature range is presented.

2. Materials and Methods

2.1 Catalyst Preparation

In this paper, a platinum promoted 20 wt.-% cobalt- Al_2O_3 catalyst is used. The catalyst was synthesized by wet impregnating 5×5 mm Al_2O_3 tablets from Sasol using cobalt(II)nitrate hexahydrate and tetraamineplatinum(II)nitrate. After impregnation and drying at ambient conditions, the catalyst was calcined by heating in the air with a heating rate of 3 K/min to 340°C and a three-hour hold at that temperature. A more detailed description of the catalyst synthesis can be found in [35]. Two subsequent impregnation steps were employed to reach the metal content of 20 wt.-%. A comparison of the catalysts used in this work and by Duerksen [33] is given in Table 1.

Table 1 Comparison of characteristic values of catalyst used by Duerksen and in this work.

	Duerksen [33]	This work
Support material	Al_2O_3	
Cobalt content/wt%.	10	21.5
Platinum content/wt%.	0.03	0.04
BET surface area/ m^2g^{-1}	180	148
specific pore volume/ cm^3g^{-1}	0.4	0.39
mean pore diameter/nm	7	7.9
Porosity	0.62	0.58
Geometry	5 × 5 mm cylinders	

2.2 Experimental Setup

All experiments were conducted in a continuous-flow fixed-bed reactor heated by an oil thermostat. The reactor was built as a single pellet string reactor, where the diameter of the reactor is smaller than two times the diameter of the used catalyst pellet ($d_{\text{pellet}} > 0.5 d_{\text{reactor}}$), allowing a reliable determination of the axial position of each catalyst pellet. For quick and easy exchange of the catalyst bed (a string of single particles), the pellets were placed in an aluminum inlay with an 8 mm inner diameter. Then, the inlay was placed inside the reactor. A more detailed description of the whole reactor concept can be found elsewhere [35].

Since FTS and HGL are strongly exothermic, particular care has to be taken to achieve isothermal conditions, especially when using a hot-start procedure. The catalyst bed inside the aluminum inlay was diluted with stainless steel grist of a diameter of around 1 mm. To prevent the catalyst pellets from floating, the pellets were weighted down by 5 mm stainless steel beads placed between every catalyst particle. Also, the aluminum inlay used proved to be very efficient in discharging the heat of the reaction.

2.3 General Proceedings

Before any FTS run, the catalyst was activated by reduction with hydrogen (15 bar, 290°C, 16 h). After reduction, the catalyst was preconditioned with ten I_{STP}/h syngas ($H_2/CO = 2/1$) at 15 bar and 190°C for 2 h, then 200°C for another 2 h, followed by 210°C and 220°C for 1 h each. For experiments at 240°C an extra preconditioning temperature step at 240°C was used, in which the synthesis was then performed for 1 to 2 h until initial methane production stabilized. After that, the catalyst pores were drained by hydrogenolysis ($p_{H_2} = 1$ bar, $p_{total} = 15$ bar, rest N_2). During the experiments presented here, no deactivation of the catalyst occurred (Figure S4), except when the hydrogen partial pressure was lower than 1 bar (partial pressure variation is not presented in this publication) but could be reactivated easily by treatment with HGL at 240°C and 1 bar H_2 partial pressure. Also, a high number of cycles periodically alternating between pore filling with FTS and pore draining with HGL did not cause any deactivation even with the number of cycles as high as 42 (at 210°C). Every Fischer-Tropsch sequence was started with empty catalyst pores and was initiated by replacing the H_2/N_2 -feed gas used for HGL with syngas ($H_2/CO = 2/1$; $p = 15$ bar) at the respective reaction temperature (210°C, 220°C, 240°C; “hot start”-conditions). Performing a hot start means exposing a completely “empty” catalyst to syngas at the designated reaction temperature. This leads to an extremely active FT synthesis and is considered the most critical part of the whole operation. Initially, the methane selectivity was high, and the reactor temperature rose by 5°C for about 20 min at 240°C set temperature, the highest measured temperature.

Carbon monoxide consumption and methane selectivity of FTS were continuously monitored with a gas analyzer and a gas flow meter. The amount of catalyst and the volume flow of syngas was always adjusted to obtain a steady state CO conversion of around 15% at any temperature. Due to the high pore effectiveness factors at 210°C, 220°C and 240°C, the initial CO conversions (after the initial phase of 45 min) are 30%, 42%, and 50%, respectively (if conversion during the initial phase is considered it can be as high as 65% at 240°C). FTS takes a long time (up to 3 weeks, depending on reaction conditions) to reach a steady state about product selectivity. Such long reaction times are not considered beneficial for the suggested alternating process, so the following “steady state” is always referred to steady CO conversion. To start the HGL reaction, the syngas feed was stopped and immediately replaced by a mixture of nitrogen and hydrogen ($p_{H_2} = 1$ bar, $p_{N_2} = 1$ bar, $p_{total} = 15$ bar, $V = 45$ I_{STP}/h). The pore-draining reaction was considered complete when the methane concentration in the product gas of HGL fell below $0.5 \text{ mmol kg}_{Kat}^{-1} \text{ s}^{-1}$. To purge the system and ensure no traces of FT product remained, pure hydrogen ($p_{H_2} = 15$ bar) was passed through the reactor prior to the following FTS run. Liquid products of FTS were collected using cooling traps at 0°C and -78°C, which were then analyzed by gas chromatographs. For analyzing gaseous FTS products, a gas collection tube in combination with a GC was used. But, since reaction times could be very short, not always enough liquid specimen was available for experimental determination of the chain growth probability (α). Thus, for the calculation of chain growth probability, the correlation of Rose was used [36]. There, α_{FTS} is calculated from the C_{5+} -selectivity. The correlation is validated for a chain growth probability between 0.6 and 0.9.

The pore-filling degree of the catalyst particles after FTS, i.e., the ratio of wax volume in the pores to the total pore volume of the catalyst, was measured using a thermobalance (TG). For this, the reactor was cooled as fast as possible and then flushed with hydrogen before the catalyst pellets were removed from the reactor. Then hydrogenolysis of the wax in the pores was conducted with

pure hydrogen at atmospheric pressure until the catalyst mass in the thermobalance was constant. For calculating the pore filling degree (F_{FTS}) from the mass change during HGL, Eq. (4) was used:

$$F_{FTS} = \frac{\Delta m_{TG}}{m_{cat,pellet} * v_{s,pore} * \rho_{wax}} \quad (4)$$

The density of the higher liquid in the pores (ρ_{wax}) was calculated using Seyer's density correlation [37]. The composition of the accumulated wax in the pores after FTS was measured by extracting the wax with toluene in a soxhlet extractor for 48 h at 73°C. After extraction, the extracted samples were analyzed by a gas chromatograph. Gaseous products of hydrogenolysis were collected using a 10 l inert foil gas sampling bag, and liquid samples were collected using a cooled (0°C) scrubber filled with toluene and a cooling trap (-78°C) behind the scrub. GC also analysed these specimens.

3. Results & Discussion

For better comprehension, the accumulation of hydrocarbons during non-stationary FTS and the consequences are discussed separately in section 3.1. The influence of hydrocarbon chain length, pore filling degree, and process temperature on hydrogenolysis and hydrogenolysis product distribution is presented after that in section 3.2. Finally, the results of the repetitive alternating cycles between FTS and HGL are compared to conventional steady-state FTS in section 3.3.

3.1 Filling of Catalyst Pores during Fischer-Tropsch Synthesis

All FTS experiments started with completely drained pores. The pores were always drained at a hydrogen partial pressure of 1 bar and the temperature of the preceding FTS run.

The key parameters of FTS over pore filling time are depicted in Figure 2. The initial phase of the FTS holds some measurement uncertainties due to the back-mixing of the product stream with the hydrogen in which the catalyst was stored while heating. The gas analyzer then measures the product stream diluted with hydrogen resulting in a higher apparent CO conversion. In order to adjust the activity, the 'hot-start'-procedure was performed but at a low temperature (40°C). At this temperature, no FT reaction is expected to happen; therefore, the influence of gas stream dilution could be measured separately. Then these values were subtracted from the originally measured curves. Figures of the correct measurements can be found in Supplementary Information (Figure S1).

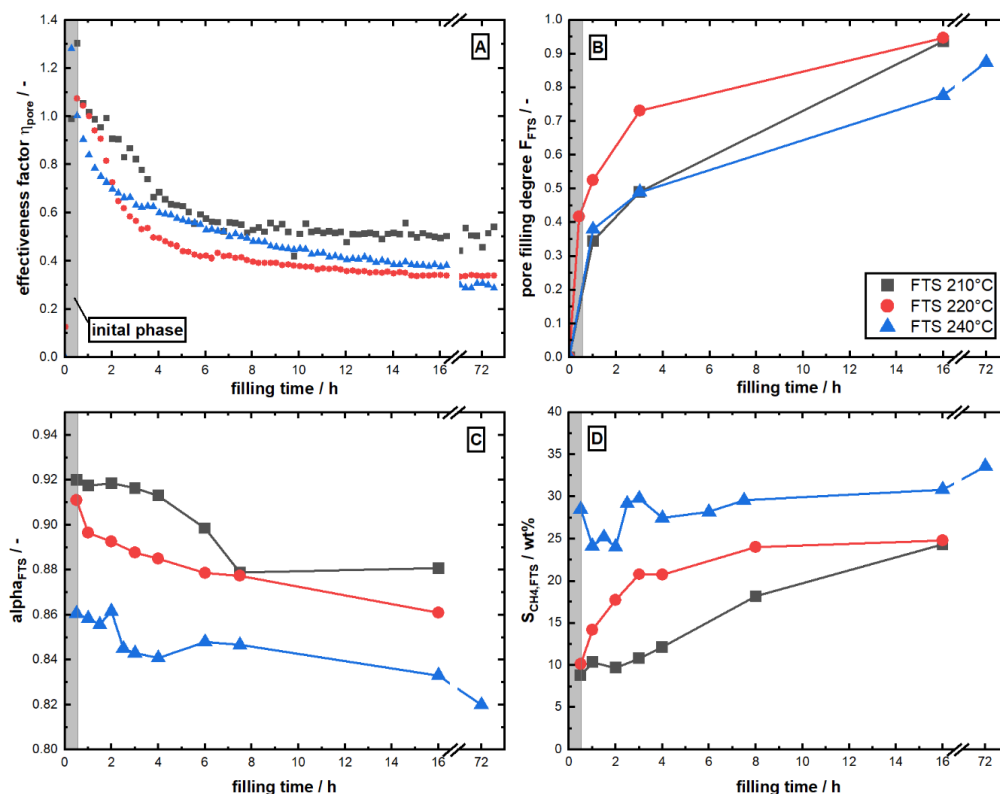


Figure 2 Progress of key figures during transient FTS ($V_{\text{syngas},210^\circ\text{C}} = 2.5 \text{ l}_{\text{STP}} (\text{g}_{\text{cat}} \text{ h})^{-1}$; $V_{\text{syngas},220^\circ\text{C}} = 5 \text{ l}_{\text{STP}} (\text{g}_{\text{cat}} \text{ h})^{-1}$; $V_{\text{syngas},240^\circ\text{C}} = 30 \text{ l}_{\text{STP}} (\text{g}_{\text{cat}} \text{ h})^{-1}$; $p_{\text{total}} = 15 \text{ bar}$; $\text{H}_2/\text{CO} = 2/1$). A) Decline of effectiveness factor over pore filling time; B) Increase of pore filling degree over pore filling time; C) Dependency of chain growth probability on pore filling time; D) Methane selectivity over pore filling time.

In Figure 2A, the adjusted curves of the pore effectiveness factor are depicted. But, even the adjusted curves show a distinct high activity at the beginning of the FTS when the pores are empty. Pöhlmann [13] showed by measurements in a magnetic suspension balance that the first layer of paraffin (a statistical monolayer is formed at a pore filling degree of about $F_{\text{mono}} = 0.2$) builds up fast in comparison with the rest of the pore filling. Measurements of the pore filling degree Figure 2B) support the presumption of extremely fast creation of a paraffin monolayer, as values for F are already well above 0.3 after only 1 h FTS at any temperature. In the further course of the synthesis, the rate of pore filling slows down noticeably, which is related to the decrease of the chain growth probability with increasing filling time and pore filling degree. The pores get filled faster despite the lower α at 220°C compared to 210°C. This is because of the higher activity of the FTS at a higher temperature. The pore-filling process is a complex combination of alkane production and evaporation. At low temperatures, α is high; therefore, a high portion of the products are long-chain hydrocarbons, which easily accumulate even though the overall production rate is low. The production rate increases with increasing temperature but α decreases. Thus, more product is made but with a lower mean carbon chain length, which then evaporates easily, and less wax is deposited inside the pores. A picture of the chain growth probability proceeding depending on the synthesis time (and therefore pore filling degree) can be found in Supplementary Information-Figure S2. The drainage of the pores resets α to the initial value due to empty pores again, and thus the mean product distribution is shifted to higher, more favourable carbon numbers.

A large quantity of liquid HCs in the pores causes a high diffusion resistance. Due to the different values of the diffusion coefficients of H_2 and CO , the H_2/CO ratio shifts within the pores to values >2 towards the catalyst core. Thus, methane selectivity increases, α decreases (Figures 2C and 2D), and the pore effectiveness factor decreases with increasing time on stream and filling degree, respectively. According to measurements made by Pöhlmann [13], the pore-filling degree has no simple linear influence on the effective catalyst activity. The first negative influence (lower activity) becomes visible at a pore-filling degree of $F > 0.5$. About $F > 0.8$ is needed to fill the transport pores in the catalyst almost completely and thus substantially decrease the effective rate of FTS.

High temperatures shift the average chain length of the hydrocarbons in the pore to higher values, as evaporation is more dominant at higher temperatures. For the same reason, the chain length shifts to higher values over time on stream, as the formation rate of the (very) high carbon number products is slower as for shorter hydrocarbons, and it takes some time for the “equilibrium” of hydrocarbon formation and evaporation to be established. This effect can also be seen in Table 2. The typical composition of accumulated higher HCs (waxes) at various temperatures and pore-filling degrees is illustrated in Figure 3.

Table 2 Overview of pore filling degree and mean carbon number obtained after different pore filling times at different temperatures and product distribution of hydrogenolysis derived from the wax residues.

	Temperature in °C	Filling time by FTS				
		0.42 h	1 h	3 h	16 h	72 h
$F_{FTS}/-$	210	-	0.34	0.48	0.93	-
	220	0.4	0.52	0.73	0.94	-
	240	-	0.38	0.49	0.78	0.87
$C_{mean,FTS}/-$	210	-	24.2	23.3	30.8	-
	220	23.6	25.8	28.0	32.2	-
	240	-	26.5	31.1	36.0	37.1
$S_{CH_4,HGL}/mol/mol$	210	-	0.46	0.55	0.66	-
	220	0.42	0.55	0.58	0.53	-
	240	-	0.31	0.43	0.45	0.49
$S_{C_2-C_8,HGL}/mol/mol$	210	-	0.21	0.16	0.17	-
	220	0.16	0.19	0.18	0.19	-
	240	-	0.12	0.14	0.18	0.21
$S_{C_9-C_{17},HGL}/mol/mol$	210	-	0.30	0.25	0.16	-
	220	0.40	0.24	0.20	0.27	-
	240	-	0.55	0.38	0.36	0.28

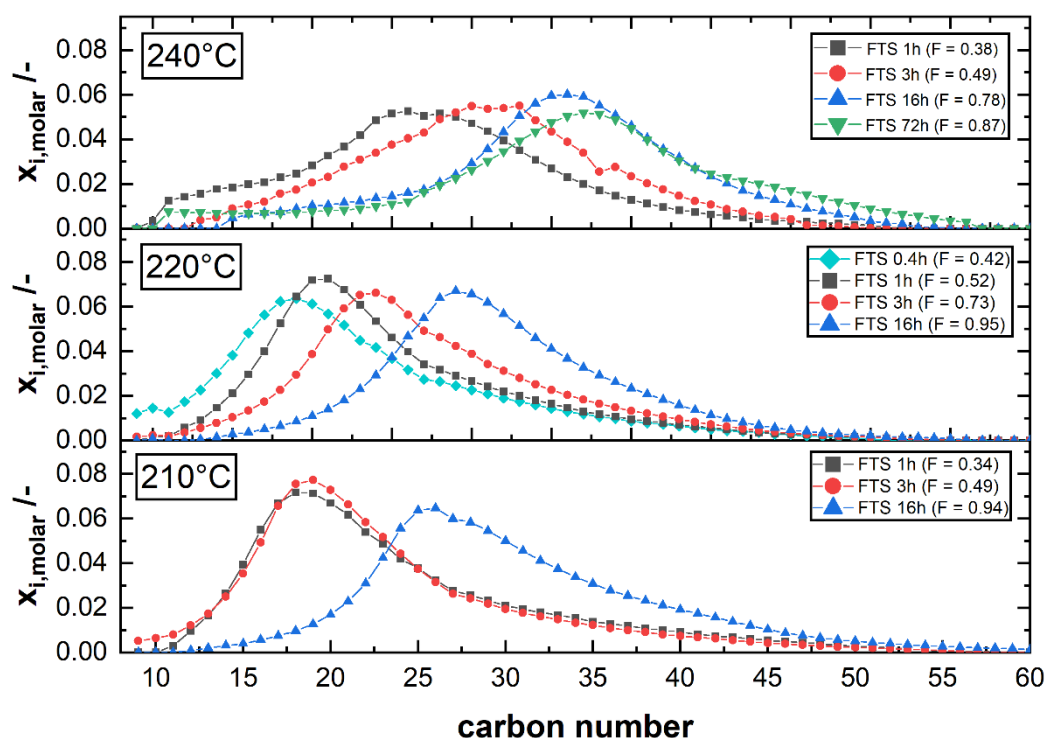


Figure 3 Composition of accumulated paraffin deposits extracted from catalyst pores at various temperatures and pore filling degrees (F).

3.2 Hydrogenolysis of Long-Chain Hydrocarbon Deposits of Fischer-Tropsch Synthesis

Since it is mostly seen as an unwanted side reaction and is not of commercial interest, the hydrogenolysis of long-chain hydrocarbons is scarcely investigated and, therefore, poorly understood. Thus, it should be noted that the pore draining by hydrogenolysis is assumed to be the result of the combination of two processes: 1) Formation of predominantly methane and, to a smaller extent, ethane and propane, thus shortening the hydrocarbon chain lengths. 2) Evaporation of the corresponding alkane, which has a higher vapor pressure due to the shortened chain length. The proceeding of the reduction of pore filling degree over time for 220°C and 240°C is shown in Figure 4. The drainage of the pores at 210°C can be found in the Supplementary Information (Figure S3).

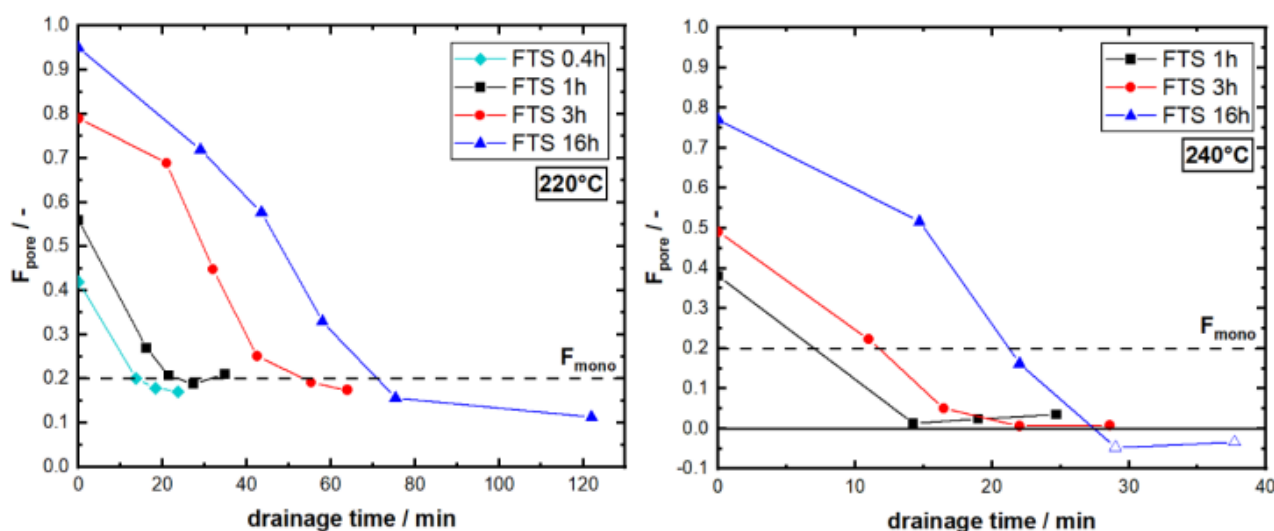


Figure 4 Decline of pore filling degree over drainage time for 220°C and 240°C ($V_{\text{HGL, total}} = 45 \text{ l}_{\text{STP}}/\text{h}$; $p_{\text{H}_2} = 1 \text{ bar}$; $p_{\text{N}_2} = 14 \text{ bar}$).

Hydrogenolysis was performed starting from different pore-filling degrees according to the time the catalyst was filled (time of FTS). Since the mechanism of pore filling is complex and currently under investigation, it is difficult to adjust the FT synthesis time so that all draining could be started from the same pore filling degree at the start, which, therefore, only roughly matches the different temperatures examined. Pore drainage progresses swiftly until the pores are fully drained at 240°C or at a rather stable pore-filling degree somewhere around the monolayer (pore-filling degree, where the layer of wax at the walls of the pores statistically consists only of one alkane molecule), as can be observed at 220°C. Extension of draining time did not affect pore filling degree, which suggests the existence of stable species on the catalyst surface, which cannot be removed at such a low temperature. The same effect was observed with experiments at 210°C, the surface could be cleaned by elevating the reaction temperature to 240°C. At 240°C, the pores can be fully drained, and no deviations compared to the different initial filling degrees are noticeable. At 220°C (and 210°C), differences between the filling times are prominent. Drainage of catalysts with a low starting pore filling degree (after 0.4, 1 h, and 3 h FTS) tend to have more liquid HCs (wax, residual pore filling degree of ca. 0.2 compared to 0.1) left in the pores than catalysts with the high pore filling degree (after 16 h FTS). As shown in the previous section, longer pore-filling times result in higher pore-filling degrees, and the composition of the liquid products in the catalyst pores shifts to a higher chain length. However, these changes appear too slight to cause such differences since this effect is also at 210°C. All subsequently performed Fischer-Tropsch experiments showed no degradation in activity, despite the only partially drained pores at low temperatures (see Supplementary Information Figure S4). It is known from the literature that hydrogenolysis can produce highly dehydrogenated deposits on the catalyst surface leading to deactivation. The tendency of deactivation increases with increasing chain length and decreasing hydrogen-to-alkane ratio. But, these deposits are easily removable by re-hydrogenation at elevated temperature and hydrogen pressure, as the hydrogen partial pressure is increased to 10 bar ($\text{H}_2/\text{CO} = 2/1$, $p_{\text{total}} = 15 \text{ bar}$) when FTS is started after 1 bar during hydrogenolysis [38-40].

The distribution of hydrogenolysis products derived from cracking long-chain HCs possesses a specific shape (Figure 5), also reported by other researchers [41, 42]. Methane is the most abundant

product of hydrogenolysis at 240°C for all measurements. The selectivity to other light alkane products of cleavage of the terminal or near-terminal bonds is comparably low, leading to the conclusion that cracking of the long-chain alkanes happens predominantly but not exclusively by successive methane elimination. Product selectivity decreases further until a local minimum is reached at a carbon number of 7. Afterward, selectivity increases again with increasing carbon number up to a local maximum at C₁₁-C₁₂. This maximum becomes less pronounced with a higher pore-filling degree. Methane selectivity decreases with decreasing pore filling degree, and the location of the local minimum remains unchanged. The same pattern is observed at 210°C and 220°C, albeit not as clearly. The methane selectivity is low for low pore-filling degrees and increases with accumulated wax. For higher pore-filling degrees, no changes in selectivity can be observed. Figures of the product selectivity obtained from hydrogenolysis at 210°C and 220°C are presented in the Supplementary Information (Figure S5). Products with a higher chain length than C₂₁ were found in none of the measurements made. Product selectivities of all HGL experiments can also be found in Table 2.

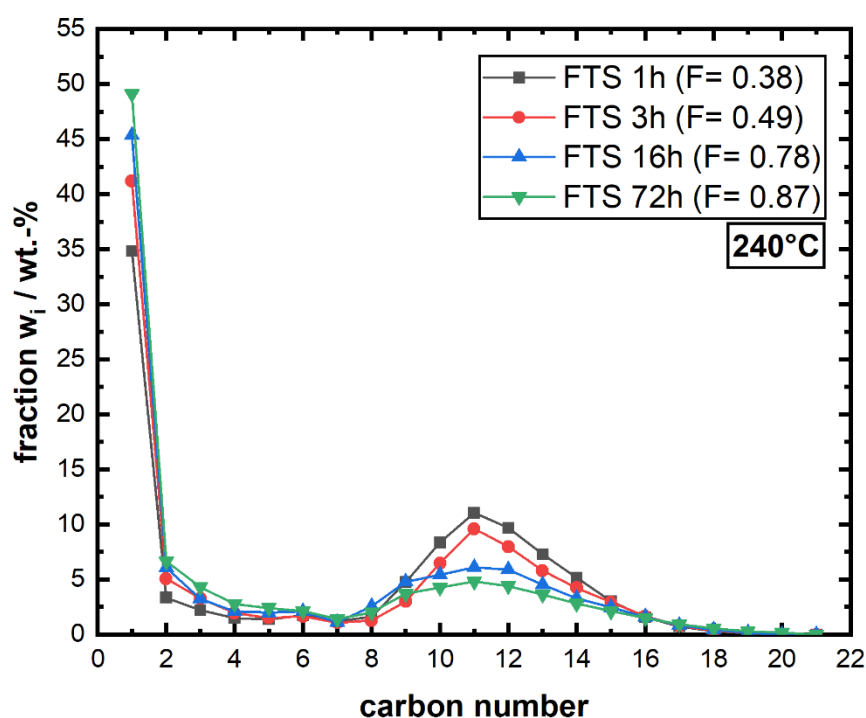


Figure 5 Typical distribution of products of hydrogenolysis at 240°C after various Fischer-Tropsch synthesis times.

The methane selectivity of the hydrogenolysis reaction depends slightly on pore-filling degree and reaction temperature. Selectivity towards C₉-C₁₇-HCs decreases to the same extent as methane selectivity increases, whereas selectivity to C₂-C₈-HCs remains mainly unchanged. C₉-C₁₇-selectivity decreases with the increasing pore filling degree but increases with increasing hydrogenolysis temperature. Methane selectivity, on the other hand, decreases with temperature. These results support the assumption that the product distribution results from methane rupture and evaporation of the longer chain HCs, once their vapor pressure is high enough. At a higher temperature, higher HCs can evaporate more easily, and therefore less methane has to be cleaved before the alkane can evaporate. Since the change of the pore filling degree always changes the

composition of the HCs present in the pores of the catalyst, no easy explanation for the dependency of selectivity during HGL on the pore-filling degree can be given. It is known from the literature that longer-chain alkanes tend to have higher methane selectivity with increasing chain length due to better stabilization of the transition state. However, this correlation is not strong [32]. For example, at 240°C, the mean carbon number of alkanes in the catalyst pores increases strongly with the increasing pore filling degree, but in hydrogenolysis, the methane selectivity doesn't change much, whereas at 210°C it is obvious that methane selectivity during hydrogenolysis increases most with the increasing pore filling degree, but at least for the first two points ($F = 0.34$ and $F = 0.48$) the product composition of the FTS waxes hardly varies. Nevertheless, it can be stated that the hydrogenolysis of Fischer-Tropsch waxes results in products with substantially shortened alkane chains and show only slight dependency on the reaction temperature and pore-filling degree, which suggests that the variation of process parameters of hydrogenolysis does not affect the alternating process by much.

3.3 Alternating Drainage of the Catalyst Pores with Hydrogenolysis after Fischer-Tropsch Synthesis

The knowledge of pore-filling behavior during transient FTS and subsequently following hydrogenolysis of the condensed long-chain hydrocarbons, gained in the previous sections, is used to enhance the overall performance of the FTS process. At this moment, pore filling time and drainage time could be identified as the two most influential factors. Here, the hydrogenolysis was conducted at the same temperature as the FTS to reduce the number of applied parameters. The drainage time depends on temperature and pore filling degree, and the pore filling degree depends on filling time and process temperature. The higher the pore filling degree, the longer the drainage time. For a better mathematical description and a better theoretical understanding Duerksen [33] introduced the process enhancement (PE) factor:

$$PE_{CO} = \frac{\int_0^{t_{FTS}} r_{CO} dt}{(t_{FTS} + t_{HGL}) r_{CO,steady-state}} \quad (5)$$

PE factors > 1 are desirable as a PE factor of one corresponds to the case that the productivity of the alternating process equals one of the steady-state processes. Since drainage time has to be considered as downtime, where no products are formed, drainage must be as short as possible. The shorter the drainage time t_{HGL} , the higher the PE factor, and for $t_{HGL} \rightarrow 0$, $PE_{CO} \rightarrow 1/\eta_{pore}$. The pore-filling degree influences drainage time, but activity is not as dependent on it up to a certain point. More specifically, the catalyst pores fill up quickly after FTS is started, but activity degrades faster only at high pore-filling degrees, leading to the conclusion that the alternating process works best within a certain time range of FTS. For $t_{FTS} \rightarrow 0$, also $t_{HGL} \rightarrow 0$ and so does the PE factor, since no FT reaction takes place.

In Figure 6A, the progress of drainage time is depicted in the context of FTS pore filling time for three different temperatures. The drainage time reaches a plateau after a certain time of FTS since pore filling happens quickly after the start of the FTS. As a certain pore-filling degree is reached, the wax deposition rate in the pore slows down and becomes insignificant for an increase in drainage time. At 210°C this takes almost 8 h, whereas at 220°C this point is reached after only 3 h. At 240°C the increase of pore filling degree is comparatively slow, and hydrogenolysis is fast, so the plateau is reached very quickly.

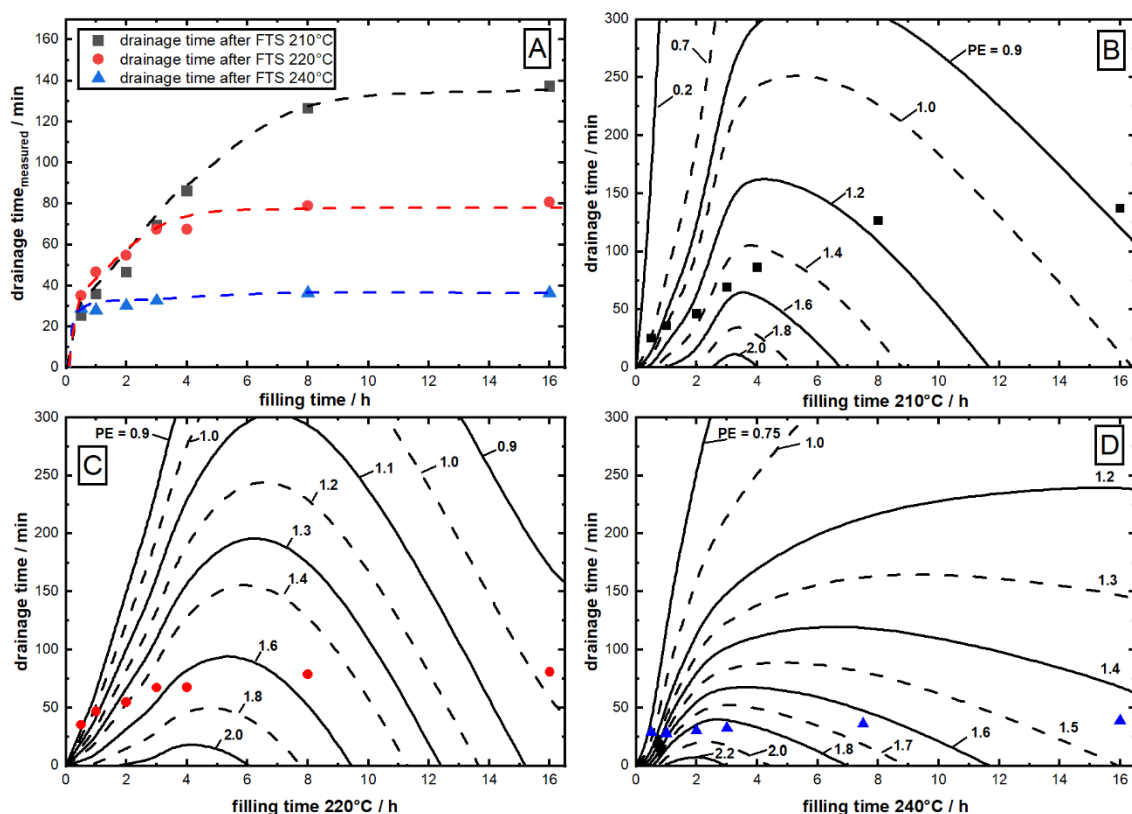


Figure 6 A) Progress of the necessary drainage measured over different pore filling times at different temperatures. B), C), D) Theoretically calculated drainage time over given Process Enhancement factors as function of pore filling time.

By solving Eq. (5) for the drainage time t_{HGL} , the set of curves of given process enhancement factors for different temperatures, presented in Figures 6B, 6C, and 6D, could be calculated. These curves give an idea of the theoretical drainage time needed for a particular filling time to achieve a certain PE factor. Shape and curvature depend solely on CO consumption and pore effectiveness factor during FTS. Higher temperatures result in higher CO consumption rates, lower pore effectiveness factors and faster pore drainage. Thus, the higher the temperature, the higher the PE factors. Interestingly, to achieve high PE at any temperature, only certain filling times appear suitable. A long FTS time on stream makes achieving a high PE factor impossible because, theoretically, negative drainage time would be necessary. The higher the desired PE factor, the narrower the field of possible cycle times becomes. A pore filling time of around 3 hours seems to be suitable for all three measured temperatures in order to achieve high enhancement factors.

Since hydrogenolysis produces mainly methane, the risk that improvements in reaction activity come along with an unfavorable reaction selectivity is high. Therefore, the process enhancement factor (PE_{CO}) is extended to PE_{C2+} , which also takes the unwanted methane selectivity into account:

$$PE_{C2+} = \frac{\int_0^{t_{FTS}} r_{CO} dt - \left(\int_0^{t_{FTS}} r_{CH4,FTS} dt + \int_0^{t_{HGL}} r_{CH4,HGL} dt \right)}{(t_{FTS} + t_{HGL}) * (r_{CO,steady-state} - r_{CH4,steady-state})} \quad (6)$$

For calculation of the production rate of C_{2+} -compounds (any FTS-product except for methane) during a cycle of pore filling and draining, the amount of methane produced during FTS and HGL is

subtracted from the amount of total used carbon monoxide during FTS and then divided by the rate of C_{2+} -production at steady state. For a better understanding of the theoretically difficult-to-access value of the $PE_{C_{2+}}$ factor, the mean methane selectivity of the alternating process (AP) is introduced:

$$S_{CH_4,AP} = \frac{\int_0^{t_{FTS}} r_{CH_4,FTS} dt + \int_0^{t_{HGL}} r_{CH_4,HGL} dt}{\int_0^{t_{FTS}} r_{CO} dt} \quad (7)$$

But, it should be noted that the addends of this equation cannot be regarded as independent since methane selectivity increases with an increasing amount of converted carbon monoxide alongside pore filling degree, which causes longer draining time and a larger amount of methane produced. Consequentially, a longer time on stream during FTS will result in a higher overall mean methane selectivity of the alternating process. The progress of mean methane selectivity proceeds as expected, except for 220°C, presented in Figure 7A. The initial maximum methane selectivity is high, which can be explained by the high activity during the hot start procedure. Then, after methane selectivity stabilizes, it increases with increasing time on stream, except for the alternating process at 220°C.

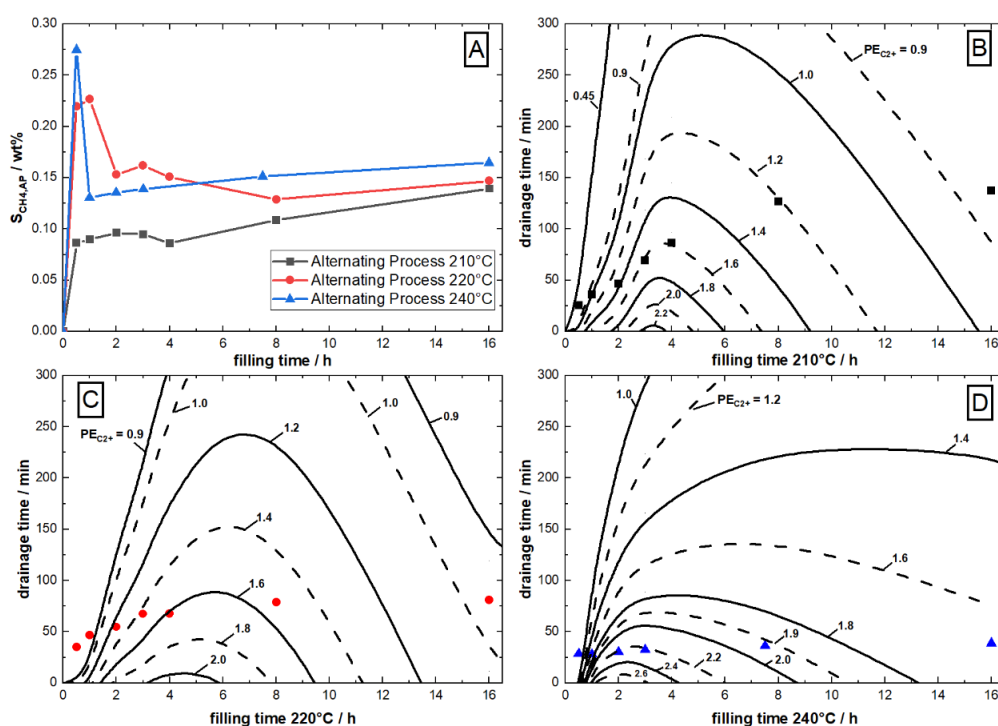


Figure 7 A) Progress of mean methane selectivity of the alternating process. B), C), D) Theoretically calculated drainage time over filling time as function of given process enhancement factors (PE with regard to C_{2+}). Measured drainage times indicated with symbols in corresponding colours for each temperature.

There, the methane selectivity is high from the beginning and decreases slowly with filling time until 8 h passes. The different operation modes of the pore filling and the pore draining can explain this. FTS is a continuous process, and the reaction rate increases strongly with increasing temperature. In contrast, hydrogenolysis can be seen as a batch or semi-batch process, where temperature influences the reaction rate but only slightly the amount of methane since the quantity

of deposited wax inside the catalyst pores is almost independent of temperature. Thus, the influence of pore drainage on the total methane selectivity of the alternating process decreases drastically with increasing process temperature. A high mean methane selectivity at 220°C is caused by a combination of a high pore-filling degree with low time on stream and an FTS activity low enough to be influenced by hydrogenolysis in pores with a relatively high pore-filling degree. So, it is not surprising that the theoretically achievable PE_{C_2+} factors (Figures 7B, 7C, 7D) are lowest for 220°C, where the theoretically achievable PE_{C_2+} value is lower than the PE_{CO} value. High process enhancement factors are not achievable for any pore-filling times. As mentioned before in the discussion of PE, a time of 3 h appears best for all three measured temperatures. The highest PE_{C_2+} was, with a value of 2.2, measured at 240°C and 2 h and 3 h.

4. Conclusion and Outlook

A potential improvement of FTS by alternating between FTS and pore draining by hydrogenolysis (HGL) is investigated and discussed. The biggest process improvement in CO conversion activity (PE) was measured at 240°C for a pore filling time (FTS time) of 2 and 3 hours and amounted to 1.9. The highest value measured regarding the activity of production of HCs other than unwanted methane (PE_{C_2+}) was 2.2, also obtained at 240°C and pore filling times of 2 and 3 hours. Thus, the assumption made by Duerksen [33] was confirmed that a higher temperature leads to higher improvement factors since hydrogenolysis proceeds with higher activity. Since temperature control is challenging in industrial applications, the alternating process was also tested at temperatures at the lower end of the LTFTS temperature scale. The results show that the FTS can be improved by alternating pore draining even at 210°C. This work clearly shows the potential of the alternating pore draining, as a clear improvement of the overall catalyst productivity by the combined FTS-HGL process is visible. Since deterioration of Fischer-Tropsch activity results from wax accumulation and, thus, a low pore effectiveness factor, alternating drainage appears as a feasible and easy option for enhancement. An increase of reaction temperature can do an increase in the hydrogenolysis rate. But, an even higher reaction temperature than 240°C may cause an unfeasibly high methane selectivity during FTS. Thus, a process with low FTS temperature and high HGL temperature is desirable, or the introduction of a more active metal on the catalyst, which possesses higher activity to hydrogenolysis than cobalt. But, improving hydrogenolysis with a bimetallic catalyst without altering the FTS for the worse might be challenging.

Author Contributions

C. Unglaub: investigation, formal analysis, methodology, visualization; J. Thiessen: methodology, project administration; A. Jess: conceptualization, methodology, supervision, funding acquisition. All the authors discussed the results and contributed to the writing of the manuscript.

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Competing Interests

There are no competing interests to declare.

Additional Materials

The following additional materials are uploaded at the page of this paper.

1. Figure S1: Progress of the CO conversion rate measured at 210°C, 220°C and 240°C. Apparent CO conversion rate is measured with the same set of process parameters except the temperature, which was always 40°C for any experiment. ($V_{\text{syngas},210^{\circ}\text{C}} = 2.5 \text{ l}_{\text{STP}}(\text{g}_{\text{cat h}})^{-1}$; $V_{\text{syngas},220^{\circ}\text{C}} = 5 \text{ l}_{\text{STP}}(\text{g}_{\text{cat h}})^{-1}$; $V_{\text{syngas},240^{\circ}\text{C}} = 30 \text{ l}_{\text{STP}}(\text{g}_{\text{cat h}})^{-1}$; $p_{\text{total}} = 15 \text{ bar}$; $\text{H}_2/\text{CO} = 2/1$).
2. Figure S2: Progress of product distribution calculated from measured chain growth probability values using Anderson-Schulz-Flory equation during the initial time of Fischer-Tropsch synthesis.
3. Figure S3: Decline of pore filling degree over drainage time for 210°C ($V_{\text{HGL},\text{total}} = 45 \text{ l}_{\text{STP}}/\text{h}$; $p_{\text{H}_2} = 1 \text{ bar}$; $p_{\text{total}} = 15 \text{ bar}$).
4. Figure S4: Comparison of FTS activities before and after pore draining using Hydrogenolysis at 210°C, 220°C and 240°C. FTS run A is measured prior to pore drainage, whereas FTS run B is measured directly after the pore drainage (full drainage, corresponds to last measuring point of the 16 h experiment visible in Figure 4 and Figure S3).
5. Figure S5: Typical distribution of products of hydrogenolysis at 210°C and 220°C after various Fischer-Tropsch synthesis time. Selectivity of methane and kerosene fraction ($\text{C}_9\text{-C}_{17}$) at different temperatures and pore filling degrees.

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