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Shell

The physics of water and wax in the pores of a working Gas-to-Liquids catalyst

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Problem definition by Shell - focal points: R. Bos, H. Geerlings, H. Kuipers and S. van Bavel

1. Abstract

The so-called Fischer-Tropsch catalysis allows to convert natural gas into liquid products and is the underlying mechanism of commercially used “Gas-to-Liquids” plants. The actual reaction takes place in millimetre sized porous pellets in which active metallic particles are dispersed as catalysts. Due to the reaction the pores of the pellets will become filled with the reaction products (“wax” and water), but it is uncertain if the fluid in the pores can be understood as a single liquid phase, a liquid-gas mixture, or multiple continuous phases. The answer to this question is important for a thorough understanding of the transport processes inside the reactor and can be utilized to improve its efficiency. In this project, a theoretical analysis of the behaviour inside the pores is performed. It is concluded that a liquid water phase might well exist next to the wax phase. However, the analysis is based on very limited experimental data of unknown quality. Therefore, we propose a number of possible experiments to validate the theoretical concepts.

2. Company profile

Shell consists of a global group of energy and petrochemicals companies with around 90,000 employees in more than 80 countries and territories. Shell is currently the largest investor in research and development among the major oil firms. In 2010 they spent around 1 billion dollars in research and development for technologies that will be needed to produce cleaner energy and more efficient fuels.

3. Problem description

In the “Gas-to-Liquids” (GTL) process natural gas – methane – is converted first into so-called “syngas” and then into liquid products – e.g. diesel, kerosine or heavier hydrocarbons – that for example can be used as transportation fuels. This process is performed commercially on a very large scale by both Shell and Sasol. These plants of Hyde Park size cost 10 – 20 billion dollar and produce up to 140.000 barrels per day. But the core of the chemical conversion process takes place on the sub nanometer scale; important physical processes take place at the scale of nano to micrometers. It is that latter scale that this problem focuses on. The chemical reaction at hand starts from the "syngas" mixture of carbon monoxide and hydrogen, which on the "active sites" of a metal catalyst reacts or polymerizes to long –linear– alkanes and water according to $n\,CO + 2n\,H_2 \rightarrow (CH_2)_n + n\,H_2O$; $(CH_2)_n$ actually being $CH_3 - (CH_2)_{n-2} - CH_3$. The conditions are $T = 200 - 250^oC$, $P = 20 - 80$bar. In practice n will be any number and hence a whole range of products are made, but for simplicity we can here assume n to be a single and high number, e.g. $n = 60$, i.e. the product is a liquid under reaction conditions. We call this product "wax". Note that for each gram of wax we approximately make 18/14 grams of water.

The wax molecules are formed on the active metal surface (the "catalyst"). In order to have a very high metal surface area the nano scale metal particles are dispersed within a porous "carrier" material. This carrier is typically in the shape of spherical, cylindrical or more complex shaped particles with a diameter of 0.1 – 3 millimeter, with an interconnected pore structure where the pore sizes are typically in the range of 5 – 100 nm.

Due to the reaction that produces both water and wax these pores will become "liquid filled". This might be a single phase of wax in which water is dissolved. In that case the gaseous components CO and H_2 flowing on the outside of the particles first have to dissolve into the liquid and then diffuse into the internal pores to reach the active sites where the reaction actually take place. Vice versa, the produced wax and water detach from the metal surface and then have to transport through the pores to the external surface of the particles. Since the reaction is fast relative to the rate of transport there will be concentration gradients of the reactants: the CO and H_2 concentration will be lower in the centre of the particle compared to the outer part. In a simple "one phase system" this also implies that the product H_2O has an inverse type of profile, i.e. the H_2O concentration – which may be zero at the outer surface – will be higher in the core and transport of H_2O primarily takes place via diffusion and a bit via convection (along with the wax that is simply being pushed out of the pores). However, this "one phase system" assumption may be completely wrong!

The key question of the project is: will there be a "simple" single wax phase inside the pores – with H_2O dissolved in it – or do we have a more complex situation, for example, a liquid-gas mixture, a micro-emulsion of water rich droplets in a wax continuous phase, vice versa wax in water, two or more different continuous phases, or something even different? Moreover, how can this be validated experimentally? And how does this affect the transport mechanisms of the reactants CO and H_2 and particularly also the product H_2O into and respectively out of the particle?

This is of imminent importance because:

- CO, H_2 and H_2O and their concentration profiles – from a metal surface perspective – will be quite different dependent on the type and nature of the phases.
- these concentrations – or chemical potentials – strongly determine the efficiency of the chemical reaction and hence the overall carbon and energy efficiency of the GTL process.

4. Problem solving strategy

The key question of this project can be rephrased by developing different "phase scenarios": simplified models of the spatial distribution of liquid water and wax in the nanopores (1). CO and H_2 are not included in these scenarios. This is reasonable, because it seems likely that no water vapor is present (see below), and that the diffusion rates of CO and H_2 through liquid

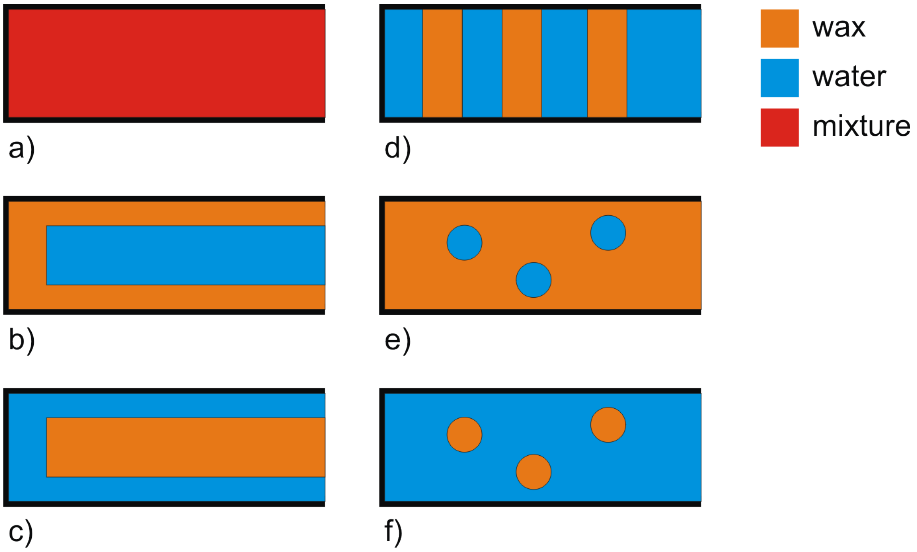

Figure 1: Hypothetical profiles of water-wax phases inside the alumina nanopore: a) a single phase homogeneous mixture, b) bulk phase separation with wax wetting the pore wall, c) phase separation with water wetting the pore wall, d) phase separation with no preferred wetting, resulting in alternating phases of water and wax, e) a microemulsion of (gaseous or liquid) water suspended in wax, and f) a microemulsion of wax suspended in liquid water. The black line represents the pore wall, with the open end of the pore on the right.

water and wax are similar. Therefore the concentration profiles of CO and H_2 in the pore are expected not to vary much between the phase scenarios.

Scenario a) is the most simple scenario, in which all water mixes on the molecular level with the liquid wax (it dissolves in the wax), creating a single continuous phase. In the other scenarios phase separation occurs between wax and liquid water. This could result in a continuous phase of wax covering the pore walls, enveloping a continuous water phase (scenario b)), or vice versa (scenario c)). Alternatively, there may be “alternating phases”, i.e. alternating pore sections filled with water and with wax (scenario d)). Finally, a (micro)emulsion of water droplets in wax (scenario e)) or vice versa (scenario f)) could occur. In scenarios e) and f), the droplets may or may not be interconnected.

Mixtures of the scenarios may occur, and the scenario may depend on e.g. pore diameter and distance to the surface of the pellet. Nonetheless, these scenarios offer a lead for further research, and can be tested numerically and experimentally. For example, scenario c) (water on pore walls) seems unlikely, because it would lead to much faster catalyst degradation than observed in situ in reactors.

Following these arguments, the project is split into two sub-tasks:

- Perform a theoretical analysis based on literature data and concepts known from classical physics to answer the following questions:
  - What is the phase of pure water in GTL reaction conditions?
  - Does all water dissolve in wax?
  - Are water bubbles/droplets stable within the wax?
  - Are water bubbles/droplets energetically more favourable than a supersaturated mixture?
- Design experiments to validate the theoretical analysis.

5. Theoretical analysis

5.1 The phase of pure water in GTL reaction conditions

For our calculations below, we will assume that in the GTL plant, a 50 bar mixture of CO (33 bar) and H_2 (17 bar) is pumped into the top of the reactor vessels. Once the gas mixture has reached the bottom of the reactor, up to 70% of it would be converted to the reaction products H_2O and $C_{60}H_{122}$. This means that the partial pressure of water in the lower part of the reactor would be around 12 bar. The temperature in the reactor is between 475 and 525K. At these conditions, bulk water exists only in the vapor phase [1].
However, due to the presence of the nanoporous pellets, we should also consider whether capillary condensation of water in nanoscale cavities is possible. The Kelvin equation [2] predicts the equilibrium radius of a condensed droplet for a fixed temperature T:

$$k_B T \ln \frac{p}{p_{sat}} = 2\gamma\nu/R_K \tag{1}$$

Here, p is the vapor pressure, p_{sat} is the saturation vapor pressure, γ is surface tension, ν is molecular volume, and R_K is stable droplet radius (actually the radius of curvature of the water interface). The surface tension of water [3] is 36.6 mN/m at 478K. The saturation vapor pressure at that temperature [4] is $p_{sat} = 19.3$ bar. For a vapor pressure of $p = 12$ bar, the equilibrium radius of a condensed droplet is -0.5nm. Since this corresponds to only 3 atomic distances, we can safely assume that, in the absence of wax, water will not condense even in the smallest cavities present.

5.2 Does water dissolve in wax?

In order to study the behaviour of water first it has to be understood whether or not the water is soluble in the wax. Therefore the questions we will try to answer is whether it is possible for the concentration of water in the wax to exceed the solubility limit during the Fischer-Tropsch (FT) process? In this section we will calculate the potential water concentration profiles as a function of system parameters and with that try to estimate whether or not water will ever exceed the solubility limit under the reactor conditions.
In order to get a qualitative feeling for the concentration of the FT reactants and products, we will model the reaction taking place in pores of millimetre size pellets using a one dimensional reaction-diffusion model. This model is just an extension to the Fick's second law of diffusion with an additional rate of reaction, which is given by

$$\partial_t c_i = D_i \partial_{xx} c_i + R_i,$$

where c_i stands for the concentration in units mol dm^{-3}, D_i is the diffusion constant, and R_i is the rate of production or consumption of species i.
From empirical evidence as well as mathematical modelling [9], it is known that the diffusion coefficient of carbon monoxide CO, is a factor of three smaller than that of molecular hydrogen H_2. The rate of the reaction equation is approximately first order in the concentration of hydrogen and zeroth order in the concentration of carbon monoxide (for sufficiently high concentrations of both reactants)

$$rate_{\mathrm{CO\ \ loss}} = kC_{\mathrm{H_2}}. \tag{2}$$

This rate equation simply expresses the fact that the binding of carbon monoxide to the catalytic sites proceeds at a much faster rate than the reaction rate between the bound carbon monoxide and the molecular hydrogen. For low enough concentrations, however, the reaction rate takes the form

$$rate_{\mathrm{CO\ \ loss}} = \frac{kaC_{\mathrm{H_2}}C_{\mathrm{CO}}}{1 + aC_{\mathrm{CO}}},$$

which shows that the depletion of carbon monoxide inside the pore terminates the progress of the reaction, however for large carbon monoxide concentrations we get the behaviour as given by 2. Here a is simply a fitting parameter.

The equation above is rather difficult to implement in the reaction-diffusion equation due to highly sensitive behaviour of the rate function, which easily leads to physically unrealistic results. For this reason we are assuming that the molar ratio of the gas present in the reactor is adjusted such that the carbon monoxide reaches further into the pellet pore, and that the concentration of molecular hydrogen is still the rate determining factor. This model is mainly meant to present an order of magnitude analysis of the concentrations, and since the diffusion rates all the gases differ by less than one order of magnitude, our assumption should be a safe one to make.

In this way, following the stoichiometric equation for alkane chains of about 60 carbon atoms in steady state $\partial_t c_i = 0_i$, we get

$$\begin{aligned} D_{H_2}\partial_{xx}c_{H_2} - 2kc_{H_2} &= 0, \\ D_{CO}\partial_{xx}c_{CO} - kc_{H_2} &= 0, \\ D_{H_2O}\partial_{xx}c_{H_20} + kc_{H_2} &= 0, \end{aligned}$$

which with the boundary conditions of $c_i\,(x=0) = c_{0,i}$ and $(\partial_x c_i)_L = 0$ (L being the depth of the pore) for i =CO, H_2O and H_2, give the following solutions

$$\begin{aligned} c_{CO} &= c_{0,CO} + c_{0,H_2}\frac{D_{H_2}}{2D_{CO}}\left(\operatorname{sech}\left(\frac{\mathrm{L}}{\xi}\right)\cosh\left(\frac{\mathrm{L}-\mathrm{x}}{\xi}\right) - 1\right), \\ c_{H_2} &= c_{0,H_2}\operatorname{sech}\left(\frac{\mathrm{L}}{\xi}\right)\cosh\left(\frac{\mathrm{L}-\mathrm{x}}{\xi}\right), \\ c_{H_2O} &= c_{0,H_2O} - c_{0,H_2}\frac{D_{H_2}}{2D_{H_2O}}\left(\operatorname{sech}\left(\frac{\mathrm{L}}{\xi}\right)\cosh\left(\frac{\mathrm{L}-\mathrm{x}}{\xi}\right) - 1\right), \end{aligned} \tag{3}$$

where the natural length scale is $\xi = \sqrt{\left(\frac{D_{H_2}}{2k}\right)}$. Here everything is working under the assumption that the reaction is taking place with the same rate constant homogeneously throughout the pore, i.e. $\partial_x k = 0$. The profiles above are shown in Figure 2.

From this model we can calculate the maximum water concentration inside the pore (at $x = L$), giving

$$c_{\mathrm{max},H_2O} = c_{0,H_2O} + \frac{c_{0,H_2}D_{H_2}}{2D_{H_2O}}\left(1 - \operatorname{sech}\frac{L}{\xi}\right),$$

where we will check whether the concentration of water is greater than the critical concentration of water that can dissolve in wax under the reactor conditions.

We estimate the carbon monoxide and hydrogen concentration at the entrance to the pore by calculating the concentration of wax present there. Since the density of wax is approximately 850 g dm^{-3}, and the molar mass of a hexacontane is about 840 g mol^{-1}, then the concentration of wax is about 1mol dm^{-3}. Additionally, at the reactor conditions (assumed to be 500 K and 50 bar) the hydrogen and carbon monoxide molar fractions are about 0.10 [9], then the concentration of molecular hydrogen at the entrance to the pore is of the order 0.1mol dm^{-3}. From the wax production data received with the assignment (100-1000 g of wax per decimeter-cubed of catalyst per hour (g dm^{-3} cat hr^{-1}), equivalent to $\approx 1.6\times10^{-4}\mathrm{mol}\,(\mathrm{dm})^{-3}\,\mathrm{s}^{-1}$), we can get that the rate of water production (equal to the rate of carbon monoxide consumption), which is of the order $10^{-2}\mathrm{mol}\,(\mathrm{dm})^{-3}\,\mathrm{s}^{-1}$. From this we obtain the rate constant $k = \frac{\text{rate of water production}}{c_{H_2}} = 10^{-1}\mathrm{s}^{-1}$, giving the characteristic length of $\xi \approx 400\mu\mathrm{m}$. For a pellet of 1 mm size, the possibly deepest pore is of the order of hundreds of

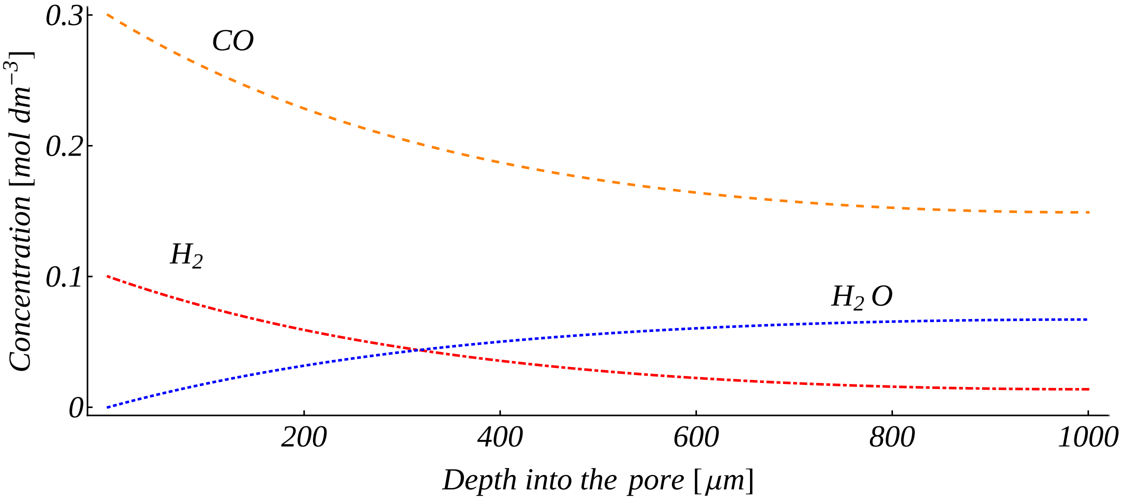

Figure 2: The profiles (solutions to 3) of carbon monoxide, water and hydrogen concentrations inside a pore.

micrometers, putting us in a regime of $L/\xi \approx 1$, with the maximum water concentration of

$$c_{\mathrm{max,H_2O}} = c_{\mathrm{0,H_2O}} + c_{\mathrm{0,H_2}}\,(1 - \mathrm{sech} 1) = c_{\mathrm{0,H_2O}} + 3.5 \times 10^{-2} \mathrm{mol\ dm}^{-3}\,.$$

A typical value for the critical solubility of water in hydrocarbons of about sixty atoms (a boiling point of about 600 K) is of the order of ≈ 60 ppm g/g or $\approx 10^{-3}$mol dm^{-3}. This an order of magnitude lower than the water concentration present inside the pellet.

5.3 The stability of water vapor bubbles in the wax

Here we try to answer the question whether water vapor bubbles can exist within the liquid wax. The pressure drop Δp that is associated with the crossing of the interface between water vapor and wax is given by the Young-Laplace equation:

$$\Delta p = -\gamma \vec{\nabla} \cdot \hat{n}. \tag{4}$$

The tendency to minimize this wall tension leads to bubbles of spherical shape (Laplace's law). Then, the above equation simplifies to

$$\Delta p = -\gamma \frac{2}{R}. \tag{5}$$

For a water vapor bubble inside hexacontane at 475K and $p_o = 50$bar, we estimated[5] a surface tension $\gamma_{\mathrm{hexacontane}} = 20\mathrm{mN\ m}^{-1}$. The pressure inside the bubble is then $p_i = p_o + \gamma_{\mathrm{hexacontane}}(2/R)$, which for a radius of $R = 25$ nm corresponds to $p_i = 66$ bar. At these conditions, bulk water will be in the liquid phase. We conclude that water vapor bubbles are unstable inside the wax in the nanopores.

5.4 The nucleation of liquid water droplets

We have concluded in section 5.2 that a mixture of water and hexacontane inside the pore would have a supersaturation factor of $W/W_{max} > 10$. We have also shown that the formation of water vapor bubbles inside the wax will be highly suppressed, since the water vapor phase is not stable at the reaction conditions. Now, we consider the nucleation of liquid water droplets inside the supersaturated state. We ask ourselves whether the formation of droplets with a radius that is smaller than the nanopore radius is energetically favourable over the supersaturated mixture state.

For the sake of simplicity, we consider the classical theory of homogeneous nucleation [6], which gives the free energy F of a liquid nucleus inside a vapor:

$$F = \gamma A - \rho_l * V * k_B T \ln \frac{W}{W_{max}} \tag{6}$$

Here, γ is the surface tension of the nucleus, A is its surface area, ρ_l is the molecular density inside the droplet, V is the volume, W is the molar concentration in the vapor, and W_{max} is the molar saturation concentration. Basically, this formula tells us that the formation of a droplet costs an energy γA to create the interface between the liquid and the vapor phase, but because of the increase of entropy, we also gain a free energy that scales with the volume of the droplet. The free energy has a maximum at the critical radius R^*:

$$R^* = \frac{2\gamma}{\rho_l k_B T \ln\left(\frac{W}{W_{max}}\right)} \tag{7}$$

Droplets that occur in the mixture are stable, and continue to grow, if they have a radius $R > R^*$. Droplets with smaller radii will not be stable and dissolve.

In order to estimate the stability of water droplets in hexacontane under GTL reactor conditions, we assume the water that is solved in the hexacontane to be a vapor. Furthermore, we disregard the free energy we have to pay in order to remove a volume V of hexacontane at the position where a droplet is formed, since the molar concentration of hexacontane is 50 times smaller than that of water. It should be noted that in this assumption, we also disregard the higher entropy per molecule of the hexacontane with respect to the water. For the interface tension between water and hexacontane we estimated a value of $\gamma_{wax-water}$ = 50 mN/m, based on values for shorter alkanes [7].

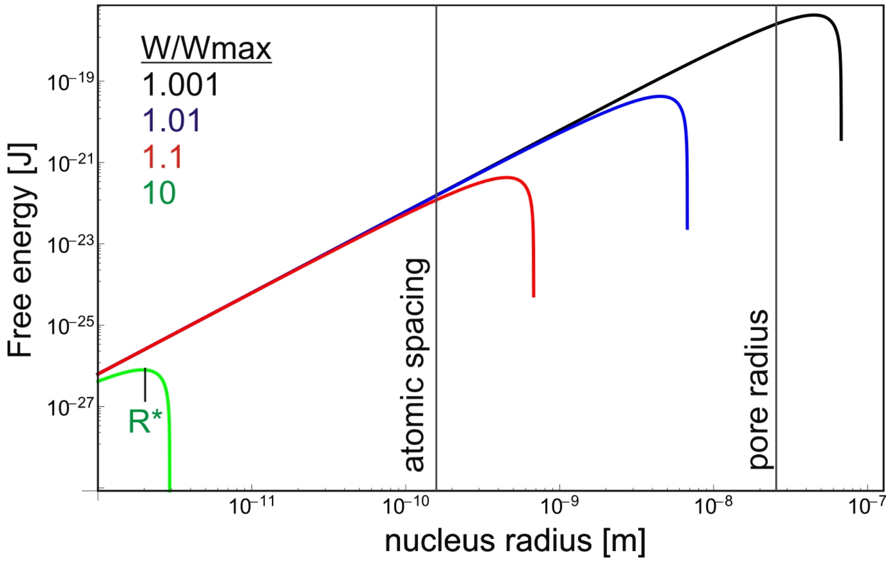

Figure 3: Free energy of nucleation versus nucleus radius for water in hexacontane at GTL reactor conditions. Note that the functions decrease quickly towards negative values for radii $R > R^*$. Because of the logarithmic scaling on the vertical axis, these negative values are not plotted.

In Fig. 3 we have plotted the free energy versus radius of a water nucleus inside the hexacontane, for several values of the supersaturation factor. For the lower estimation of W/W_{max} = 10, we obtain a critical radius of 2pm, which is much lower than the atomic spacing

between water molecules. Since the supersaturation in reality is even larger, we conclude that the water droplets can easily be formed.
The mass production rate of water and wax is almost equal, and these two have nearly the same mass density. Therefore, during the process, we have approximately equal volume production of wax and water in the pore. A possible scenario for the demixing inside the pores is that we have alternating layers of the wax and water, perpendicular to the pore wall, with almost equal volume, which move towards the exit point of the pore. This scenario is illustrated in Fig. 4 for two cases: 1) water is wetting on the Alumina pore wall, or 2) water is non-wetting on the pore wall.

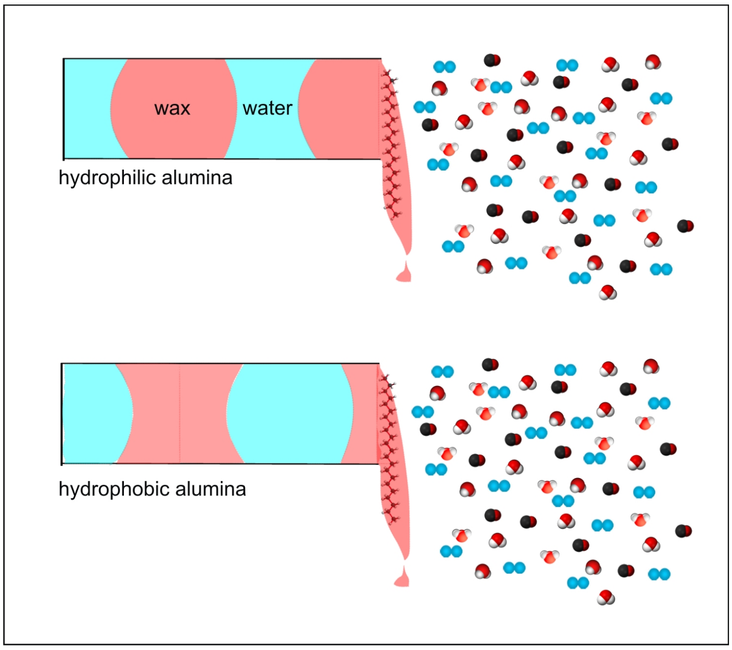

Figure 4: Two possible scenarios for the demixed water-hexacontane structure inside the alumina nanopores: Water is non-wetting on the alumina (top), and water is wetting on the alumina (bottom)

Observations on alumina that is used inside the GTL reactor are reported to show that the surface tends to become non-wetting for water during the reaction. This could be due to the adsorption of hydroxides on the pore walls. Non-wetting of water would lead to a layer of hexacontane on the pore walls, which is in agreement with the observation that the catalyst particles, in the steady state of the process, are not oxidizing fastly as they seem to do when in contact with bulk liquid water.

6. Proposed experiments

This section is devoted to experimental methods to probe the physical situation within the porous medium where the Fischer-Tropsch (FT) reaction takes place (see the phase scenarios in Figure 1). In the preceding sections it was clear that some bulk physical parameters are necessary to do modelling of the system in order to discriminate between various possible scenarios. Additionally, some model systems are proposed that mimic the inside of the pellet but offer more control of experimental conditions, giving a view on the non-equilibrium steady state present near catalyst sites.
This section is organised as follows. We first list the crucial bulk parameters needed to get a basic model of the system. Then we describe different (model-) systems for later reference when we discuss various experimental techniques.

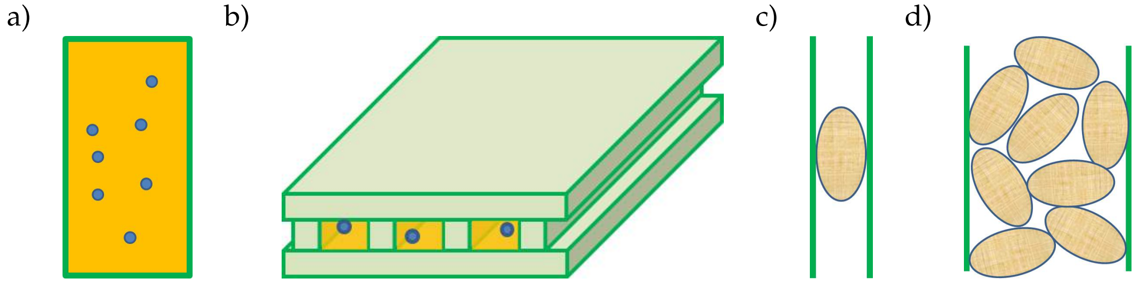

Figure 5: (Model) systems. (a) pressure cell, (b) array of nanochannels, (c) single pellet in sample cell, (d) reactor system: a tube filled with pellets.

Bulk parameters are associated with the equilibrium properties of the system. In the non-equilibrium system (active reactor), these parameters play a crucial role in the understanding of and discrimination between different non-equilibrium processes. The parameters can be measured in absence of the FT reaction (but at reactor pressure and temperature) and without the complications of measuring inside the porous medium. For simplicity we refer to the porous medium as Al_2O_3.

- *Surface tensions* between H_2O/Wax and Al_2O_3/H_2O and Wax/Al_2O_3. Surface tensions should be measured both for liquid water and for water vapour. These surface tensions determine the nucleation radius of water droplets within the wax and determine the contact angles and wetting phenomena that determine if the Al_2O_3 surface is covered with water or wax. The Al_2O_3 may (in time) become covered with a layer of alcohols and carboxy-acid FT by-products, which will strongly affect the surface tensions, which should therefore also be measured in this Al_2O_3 state.

- The *Solubility* of H_2O in Wax, and for detailed analysis also CO and H_2 in liquid H_2O and Wax.

- *Diffusion Coefficients* of dissolved H_2O, CO and H_2 in wax, and CO and H_2 in liquid H_2O.

We propose several (model) systems for the experiments in the next section, see Fig. 5.

- Bulk wax and water, e.g. in a pressure cell, to measure the equilibrium properties described above under reactor conditions (Fig. 5a).

- Nano-channels: an assembly of parallel nanochannels, e.g. by etching channels in a glass plate, coating it with a thin layer of Al2O3 and covering the glass plate with a second plate (Fig. 5b).

- Single pellet in sample (flow) cell under reactor conditions (Fig. 5c).

- Reactor system: a tube filled with pellets, under reaction conditions (Fig. 5d). This system is the most heterogeneous, and therefore least simple to experiment on. However, it may yield the most representative information for what happens in situ in a reactor. Moreover, this system contains a large amount of all material, which may be crucial for experiments with weak signals, such as electron paramagnetic resonance (see below).

6.1 Methods

In this section we list possible approaches to probe the relevant physics inside the pellets. Note that we focussed on providing a range of creative solutions, that have to be worked out in future work.

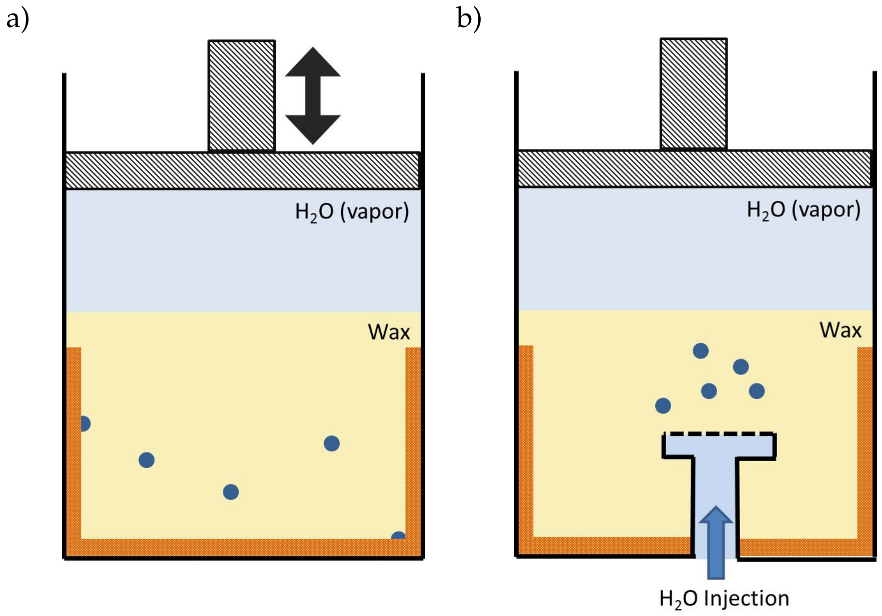

Figure 6: (a) Proposed pressure-jump setup, to study non-equilibrium processes, such as bubble/droplet formation. (a) Wax becomes oversaturated with H_2O by moving the piston up (releasing vapour pre ssure). (b) Injection of H_2O in the setup mimics the continuous generation of H_2O by the FT reaction.

Pressure jump experiments

Two methods of creating and studying water bubbles/droplets in liquid wax in a controlled way is illustrated in Fig. 6a. A pressurized cylinder filled with liquid wax is in equilibrium with the water vapor above it, at pressure p_i, where the amount of water dissolved in the wax is determined by the Henry constant. Releasing the piston (or a valve) to reduce the pressure to p_f ($p_f < p_i$), will lead to over saturation of the water in the wax. Consequently water will move out of the wax, through diffusion, bubble fo rmation and/or droplet formation. The water movement could be measured with a range of methods (imaging, scat tering, spectroscopy), provided the cylinder is transparent. This would yield information on several important bubble/droplet properties: the location and number of nucleation sites, the rate of nucleation, speed of mo vement along the surface/through bulk wax, number of bubbles/droplets and their size distribution. This measurement system enables studying the individual effect of several "actors" which all act simultaneous ly in the pellets, such as the extent of oversaturation, the nature of the pore surface (Al_2O_3, or Al_2O_3 covered with FT (by)products), and the presence of syngas at different concentrations. An extension of the system includes a nozzle in the cylinder wall (Fig. 6b) to inject water vapor at a controlle d rate (mimicking water production at the catalytic sites). This may offer a way of measuring a critical injection rate leading to liquid water phase in the wax. Adding catalysts is another way of producing water in th e cylinder, but this has the disadvantage that the effect of CO and H_2 concentrations cannot be varied indep endently from the water production rate.

^{1}H-NMR diffusion measurements

The T_2 relaxation time of the protons of water in small droplets is determined mainly by the average time for a water molecule to diffuse to the interface with the wax. Thus T_2 measurements can be used to estimate droplet radii, provided the diffusion coefficient of water is known. The droplet size inside nanopores may be too small (too short T_2) to be detectable by standard NMR T_2 methods [12]. Before experimenting, it is therefore recommended to estimate the minimal detectable droplet radius, which depends on the time-resolution of the NMR apparatus. Dedicated pulse sequences may increase the radius/time resolution [13]. Detection of bubbles of water vapor is probably much more difficult, due to the low proton density and the higher diffusion coefficient than liquid water, which increases the minimal detectable radius. The ferromagnetic cobalt catalyst will cause inhomogeneities of the magnetic field, leading to fast T_2 relaxation. For low catalyst densities in the pellets this may not be a problem; it will render the water molecules in close proximity of the catalysts undetectable, without effecting the T_2 of the water at longer distances. For high catalyst densities the cobalt catalyst has to be replaced by a paramagnetic ruthenium catalyst, although this may render the experiment less representative for what happens in an active reactor.

Dielectric constant

Dielectric spectroscopy measures the complex relative permittivity for a wide range of frequencies from Hz - THz. The complex relative permittivity is given as $\epsilon = \epsilon' - i\kappa/\epsilon_0\omega$ where ϵ' is the relative permittivity, κ is the conductivity, ϵ_0 is the vacuum permittivity and ω the angular frequency. The real part of the complex relative permittivity ϵ' will show up as a phase shift in dielectric spectroscopy and the imaginary part is associated to attenuation of the signal. The dielectric constant of single-phase systems depends on its molecular properties. However, for an emulsion consisting of water and oil with complex dielectric constants ϵ_w and ϵ_o, there will be Maxwell-Wagner-Sillars polarization at the boundary between the two media. This opens the possibility to study the properties of the emulsion [10].
The catalyst particles will probably interfere strongly with the dielectric measurements. But one could study a single pellet or the nano-channel setup by appropriate subtraction of the background signal.

Markers

The presence of liquid water at the pore surface could be probed by (sparsely) attaching a "marker" on the pore surfaces. When the marker is in contact with liquid water it should give a lasting response, but not in the presence of water vapor or dissolved water. An advantage of this approach is that the response can be measured offline, i.e. post-FT-reaction, outside the reactor and under ambient conditions. This greatly increases the number of techniques to probe the response, e.g. examination of pellet slices with electron microscopy. It may be necessary to use secondary markers such as such OsO_4, to selectively label the response area. We propose two categories of markers:

- *Conditionally mobile markers* are only mobile in the presence of liquid water. Suggested markers are (i) small water soluble salt crystals, (ii) compounds that strongly binds to the pore wall via multiple hydrogen bonds (H_2O-sensitive covalent bonds with the walls are unsuited, because they are probably also sensitive to dissolved H_2O), and (iii) cobalt particles that are too small to be active catalysts (such particles may even form fresh active catalytic sites via Ostwald ripening, providing a means of replenishing degraded catalyst particles). The presence of liquid water would lead to detectable spatial redistribution of the markers, starting from either a spatially homogeneous distribution of markers, or from an inhomogeneous distribution.

- *immobile markers* lead to a local (and lasting) response in the presence of liquid water, e.g. chemical/physical changes of the pore wall or of the marker itself.

This quality of the marker makes or breaks this type of experiments. A good marker has to meet several requir ements:

- *Stable* under the reactor conditions
- *Non-interfering* with the FT reaction and movement of reactants and reaction products. Interference could be chemical but also physical (e.g. steric hindrance). This requirement probably implies using low labelling densities. In view of the offline measurement of the response this seems to pose little limitation. Interference should be checked by comparing the FT reaction rate in presence and absence of the markers.
- *High selectivity*. The markers should have high contrast ratios for response to liquid water and the other phases/compounds present in the pores. Selectivity could be checked on model systems, e.g. Fig. 5a,b or on a flat surface of Al_2O_3 covered with markers.
- *Suitable sensitivity*. The sensitivity should be such that the inverse response rate is of similar magnitude as the typical exposure time of the marker to liquid water.

The markers described above have the advantage of measuring offline. Ideally a response would be measured in situ, in an active reactor. This limits the measurements techniques, and therefore the marker types. One measurement that may work is the detection of spin labels detected by EPR (electron paramagnetic resonance). The line shape of the EPR spectrum is sensitive to the mobility of the label, which depends on its local environment. It may therefore be used to distinguish between liquid water/liquid wax/water vapor. EPR spectroscopy has been demonstrated on substrates bound to porous Al_2O_3, albeit at ambient temperature [14]. In the ideal case spin probes could be attached to the pore surfaces via different lengths of stiff linkers, and consequently probe the local environment at difference distances from the pore surface (distinguishing e.g. between Figure 1b and c). The EPR marker-response experiment is particularly challenging, because:

- *Unpaired electrons* of the spin labels, may be chemically active under reactor conditions.
- *Labelling density* required for sufficiently strong EPR signal may be prohibitively high and interfering with the FT process.
- *Cobalt catalyst* may interfere with EPR experiments, as also expected for the NMR experiments, in which case it should be replaced by ruthenium.

Isotopes

The average time H_2O molecules spend within the pellets depends on their mobility. This mobility will differ significantly for H_2O dissolved in wax, a water-in-oil emulsion and a percolated network of water. In order to measure the average dwelling time of H_2O molecules within a pellet we propose the following methodology. For water dissolved in wax and percolated water networks the mobility will be determined by the diffusion constants of water-in-wax and water-in-water respectively. For the emulsion the droplet size will play a role since larger droplets will be less mobile than smaller droplets via Stokes' law.

We propose the following methodology. Inject syngas with one isotope taking the place of hydrogen, oxygen or carbon. The syngas will diffuse into the pellet and the FT-reaction will form H_2O and Wax containing the isotope we injected. For simplicity we assume the FT reaction is insensitive to the isotopes. After the reaction all carbon isotopes will end up in the wax, all oxygen isotopes will end up in the water and deuterium the isotope of hydrogen will end up 50% in wax and 50% in water. In a time-resolved measurement of the concentration of isotopes ejected from the reactor different timescales will show up, see Fig. 7.

There will be a timescale associated to the diffusion of syngas through the reactor. This will cause the pulse of isotope concentration released to be detected slightly later and a broadened with respect to the injected pulse of isotope concentration, even in the absence of the FT

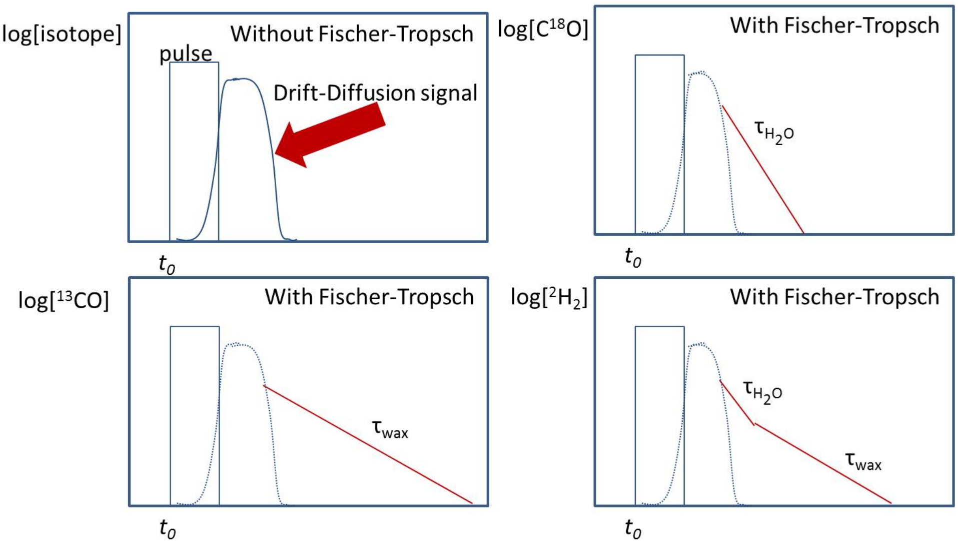

Figure 7: Sketch of the isotope concentration as a function of time. At $t = t_0$ a concentration of an isotope is injected in the reactor. After drift and diffusion through the reactor the isotope appears at the other side of the reactor. The pulse has slightly broadened due to diffusion (top left figure). The other subfigures show the decline of the various isotope concentrations ejected from the reactor and the associated timescales due to different mobilities associated to the reaction products that the isotopes become.

reaction. The lower mobility of the wax will result in a longer timescale for the isotopically marked carbon atoms than the timescale for marked oxygen which will end up in the water. Using various isotopes to mark the carbon, hydrogen and oxygen one would in principle be able to disentangle different diffusion coefficients for the syngas entering the pellet and may even detect more timescales associated to the ejection of water from the pellets which would hint at combined diffusion by some dissolved single molecules and droplets of liquid water.

Opto-Acoustic

We propose to use a pulsed laser beam to heat the liquid water generated in the porous structure. The proposed methodology is used in medical diagnostics and is capable of determining microemulsions in biological tissue[15]. The water will show a thermoelastic expansion and pressure waves will be emited giving an acoustic signal. The relevant physics is summarized in the equation

$$\left(\nabla^2 - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right)p(x,t) = -\frac{\beta}{C_p}\frac{\partial H}{\partial t}, \tag{8}$$

where $p(x, t)$ is the pressure field, H is the heat deposited in the medium per unit volume and time, v is the speed of sound in the medium, β is the thermal expansion coefficient and C_p is the heat capacity at constant pressure. The propagation of acoustic waves depend on droplet size and bulk properties of the wax and water[11] and can be detected via ultrasound transducers. We think this approach is feasible due to the large absorption of IR radiation by liquid water at a wavelength 2.9μm. The wax does not absorb much radiation in the infra-red and also the Al_2O_3-pellet scatters the light but does not absorbs the radiation so heating of the Al_2O_3 is limited.

Moreover, even if all components in the pellets would heat due to the applied laser power, the thermoelastic response of liquid water droplets probably is much stronger than the expansion of the wax. Providing us with a clear signal.

Diffusion of inert Gas

The diffusion rate of an inert gas through a pore filled with the FT mixture offers a way to probe the presence of liquid water and water bubbles, by measuring the transition time of a brief pulse of inert gas from one end of the pore to another. For an inert gas with identical diffusion coefficients in liquid water and in wax, the diffusion time through the pore depends on the fraction of water bubbles. In the absence of water vapor bubbles, an inert gas should be used with different diffusion coefficients in liquid water and liquid wax. The diffusion time of such an inert gas through the pore will depend on the fraction of liquid water. For both types of inert gas, the (distribution of) transition times depend not only on the volume fraction of bubbles/droplets, but also on their mesoscopic "structure" and size: An interconnected network of bubbles/droplets may offer "highways" for the inert gas movement, resulting in short transition times. A large number of small bubbles/droplets may result in different diffusion times than the same volume fraction of larger bubbles/droplets. The net results of these effects unknown a priori, but can be assessed through simple 1 or 2 dimensional diffusion models.

Bubble exit from pores

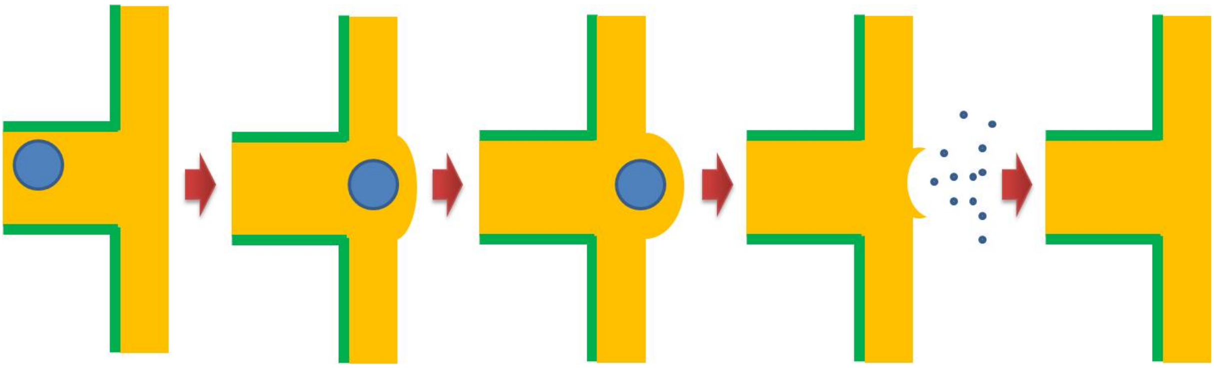

Figure 8: Scenario for a bubble/droplet (blue) exiting a pore by breaking through the film of wax that covers the pellet (yellow).

The presence of water bubbles/droplets may be assessed from their exit from the pores. In a reactor the outer surface of each pellet is covered by downward flowing wax. Water exiting a pore has to travel through this file of wax. This can occur by (i) diffusion through the wax, (ii) a vapor bubble erupting at the surface, and (iii) a liquid droplet arriving at the film, where it evaporates due to the low water vapor pressure outside the pellet. Diffusion will leave the surface shape of the film unaffected. By contrast, bubbles and droplets will lead to a deformation of the film, followed by rupture ("popping") of the film (Fig. 8). Several experiments can distinguish between these two cases.

- *Shape distortion* measured by changes in light scattering properties of the film or by changed reflection/deflection of laser beam by the wax film.
- *"Popping of bubbles"* measured from the resulting acoustic wave.

These types of experiments rely on detecting single droplet/bubble exit events (detecting multiple events simultaneously results in a smeared out signal, which is expected be very similar to that of respect to exit via diffusion). Single exit event detection requires a

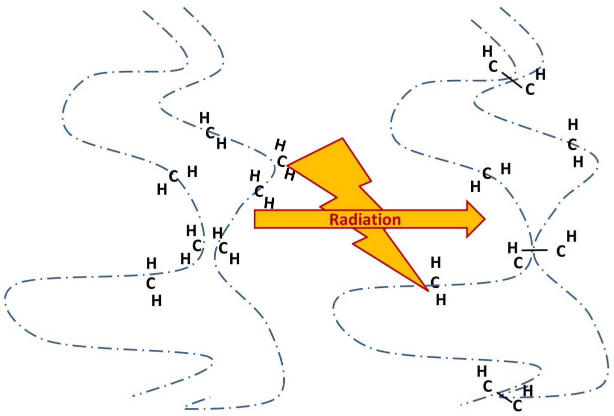

Figure 9: Exposure of the alkanes to ionizing radiation will cause the instant formation of crosslinks[16], thus creating a more rigid structure that keeps its structure in ambient conditions allowing for a range of standard microscopy techniques to probe the distribution of water pockets in the system.

time-resolution better than the average time between two events. It may be necessary to reduce the rate of exit events by measuring on single (or small numbers of) pellets, or by reducing the number of pores per pellet. Optical methods probably yield higher time-resolution than acoustic methods, because acoustic waves may experience more dispersion.

Quench

In the preceding sections we showed that we expect liquid water and wax to fill the pores of the pellets. Nucleated water droplets would coalesce and could form percolation networks of liquid water inside the pores. If this theory is valid, one way to observe these networks or droplets woud be by quenching the reaction in such a way that the water or wax cannot redistribute during and after the quench. We thought of two possible quenching techniques which we list below. After quenching the structure of the percolated network of wax would be visible using for example electron microscopy of a slice of the pellet. The quenching possibilities are

1. *Freeze* the pellet by cooling it fast to a temperature at which the wax solidifies. A problem with this approach is the liquid water in the pores would expand and the structure after the quench would not be representative for the structure under operating conditions.
2. *Irradiate* the sample such that the alkanes in the wax cross-link and form a strong network that fixes the wax. As illustrated in Fig. 9.

6.2 Suitability of experiments for model systems

To summarize we made a table showing the viability of the sketched methods for the different model systems. The Pressure jump experiments need to be done in the cylinder-piston geometry. For the other methods we refer to table 1.

7. Conclusions

The aim of this study was to understand the physical state of water in porous catalyst particles during a Fischer-Tropsch reaction. Does water mix with the wax produced in this reaction or

experiment	nano-channels	single pellet	minireactor
1H-NMR diffusion measurements	+/-	+	+
Markers	+	+	+
Diffusion of inert gas	+	+/-	-
Bubble exit from pores	+	+	-
Dielectric constant	+	+/-	-
Isotopes	+	+	+
Thermo-Acoustic	-	+	+/-
Quench	-	+	+/-

Table 1: Feasability of the methods in the different model systems.

does a second phase develop? And if a second phase develops, what is the nature of this phase: a vapor bubble or a water droplet. By analysing the 1D reaction-diffusion equations it was shown that in the operation window of the reactor water always exceeds the solubility limit. So, the formation of a second water rich phase seems plausible. At this point it has to be remarked that there is little quantitative data on the mixing behaviour of water and wax at the pressures and temperatures of interest. On the basis of thermodynamic analysis it was proven that water will not form gas bubbles, but preferentially nucleates in droplets. At the given process conditions nucleation of these droplets is possible within the porous matrix of the catalyst. In order to come up with more reliable prediction of droplet formation there should be more quantitative data on the surface tension of the wax/water interface at the processing conditions. Further, it seems that the formed droplets are more stable in the core of the pellets than at close to the external surface of the pellet. However, the stability of a water droplet in relation to its location in the pellet deserves more attention. The same is true for the motion and aggregation of the droplets inside the pore system. The conclusion that water does not mix with wax and forms a separate (liquid) phase seems to be contradictory with experiences with respect to the life-time of the Co-catalyst. In general Co-particles quickly deteriorate in water at the given temperatures and pressures, but this does not happen in the so fast in the reactor. Possible explanation could be that the wax that grows directly on top of a Co-particle actually protect the particle from attacks by liquid water.

An important conclusion of the presented study is also that the theoretical analysis has to be built on a small amount of experimental data of unknown quality. The problem is that there is little information on the water/wax phase behaviour and the surface properties of the water/wax interface at high temperatures and pressure. Therefore, it is concluded that proper validation of the theoretical concepts discussed in this paper is only possible when more experimental data is collected. High quality experimental data of the phase behaviour of water/wax are the key to breakthrough in our understanding of the wax/water distribution in the porous catalyst. To validate the idea of droplet formation an experiment is proposed to monitor the birth and growth of droplets at the catalyst particles during the reaction. Further various techniques are proposed that are capable of identifying liquid water in situ in a Fischer-Tropsch reactor.

In summary, it has to be concluded that the presented analysis points to the presence of a co-continuous network of wax and liquid water in the porous pellet. Key to progress is high quality data on the wax/water phase behaviour.

8. Outlook

As an outlook we would like to propose PhD projects that could be carried out by a prospective student at a physics or chemistry department. This research projects were thought up based on the conclusion of the research conducted during the workshop week.

One of the possible PhD project could involve building a more accurate mathematical model which would attempt to describe the *local* dynamics of composition fluctuations inside the pore. On the scale of tenths or hundreds of nanometers, one could study the creation and dynamics of two phases (water and wax, perhaps even with its composition modelled by the Anderson-Schulz-Flory distribution). This model could analyse whether one would indeed see phase separation, with nucleation of water droplets. One could also include in said model spacial differences in catalytic synthesis conditions which give rise to different product formation.

First this will be studied on pore-to-pore basis. Secondly, the outcomes will be scaled-up to the pellet and reactor level to be able to calculate experimentally as well as industrially measurable effects on the FT synthesis.

A second possible PhD project involves to perform some of the experiments which were proposed during the workshop. This is will allow to collect high quality data on the surface tension between wax and water, the solubility of water in wax, or the corresponding diffusion coeeficients. These findings could then be used by the first PhD to improve the theoretical models.

The third PhD project we propose involves computer simulations. By using molecular dynamics together with simplified models for the chemical reaction itself, the transport of reaction products and their phase behaviour can be studied on the single pore level. In order to upscale the obtained results, we propose to combine the microscopic simulations with continuum multiphase fluid dynamics simulations to understand the transport of water and wax on the pellet- or reactor level.

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