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Opportunities for intensification of Fischer-Tropsch synthesis through reduced formation of methane over cobalt catalysts in microreactors

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Due to the global growth in production of synthetic fuels via the Gas-to-Liquid (GTL), Coal-To-Liquid (CTL) and Biomass-To-Liquid (BTL) processes, both academic and industrial interest in the Fischer-Tropsch Synthesis (FTS) research has increased during the past decade. The undesired product of FTS is methane and it is formed in amounts higher than expected according to the current understanding of FTS mechanism. Therefore, it is important to gain better understanding of methane formation in order to optimize the FTS process. In this review we discuss the reasons responsible for higher than expected methane selectivity under FTS conditions over cobalt-based FTS catalysts and describe novel microreactors for use in FTS. These novel reactors could help improve reaction selectivity and yield, as well as offer significant economic benefits. Recommendations are given for intensification of FTS in terms of product selectivity by improved selection of catalyst, process conditions and reactor configuration.

Fischer-Tropsch synthesis technology

The renewed interest in conversion of syngas into hydrocarbons using Fischer-Tropsch synthesis (FTS) is principally due to the concerns about rational use of fossil and renewable resources. Both fossil and renewable resources can be converted into liquid fuels using XTL (X-To-Liquid) technologies, where X can be natural, associated or shale Gas, Coal or Biomass. Significant reserves of natural and shale gas in several countries (e.g. Qatar, Malaysia, Nigeria and USA) have made it attractive to construct refineries that operate using FTS technology. Natural and shale gas is mainly composed of methane, but it also contains carbon dioxide, light hydrocarbons (C_2 - C_4) and other impurities. Indirect routes for natural gas conversion are multi-step processes in which methane is first converted into syngas (a mixture of carbon monoxide and hydrogen). The success of indirect conversion is due to the ease of conversion of natural gas into syngas, and to the multitude of products (hydrocarbons, oxygenates etc.).The indirect conversion of natural gas is realized in industrial units of large capacity (more than 120 million tons per year).

The Gas-To-Liquid (GTL) technology is a complex process which consists of several reaction steps (Figure 1): (a) conversion of natural gas into syngas using steam reforming, partial oxidation or autothermal reforming; (b) syngas conditioning, adjustment of H_2/CO ratio and cleaning; (c) conversion of the syngas to liquid hydrocarbons via the FT synthesis; (d) conversion of liquid hydrocarbons into final products via hydrocracking and/or hydroisomerization. The CTL and BTL processes convert respectively coal[1, 2] and biomass[3-6] into synthetic liquid fuels. These technologies involve coal or biomass gasification, followed by syngas purification and H_2/CO ratio adjustment via water gas-shift (WGS) reaction. The syngas is then converted into liquid hydrocarbons using FTS.

The heart of the GTL, BTL and CTL processes is the FTS reaction in which syngas is converted to hydrocarbons over a cobalt or an iron catalyst. Cobalt is the catalyst of choice for low temperature FTS and high H_2/CO feed ratio (GTL application), due to its high activity and selectivity towards desired products, as well as the absence of water-gas shift reaction.[7] Iron based catalysts are used to process coal derived synthesis gas (low H_2/CO feed ratio), due to their ability to generate H_2 internally via the WGS reaction. Overall stoichiometry of FTS can be presented as:

$$CO + (1 + \frac{m}{2n}) H_2 \xrightarrow{r_{FTS}} \frac{1}{n} C_n H_m + H_2O \qquad (1)$$

During the reaction a mixture of hydrocarbons is created, from methane to hydrocarbons having over 100 carbon atoms in a molecule. The selectivity of FTS product formation over the active catalyst surface is a function of the reaction conditions. In order to make the XTL processes cost-effective, the amount of low carbon number products, which cannot be used as liquid fuels, has to be minimized. In particular reduction of the amount of methane, as the most undesired product, is of the utmost importance.

There are two general types of FTS technology that are currently employed on a commercial scale: high and low temperature Fischer-Tropsch (HTFT and LTFT), where the latter is typically used in the industry for synthesis of liquid fuels.[8, 9] LTFT is characterized by three-phase operation and is mainly conducted in

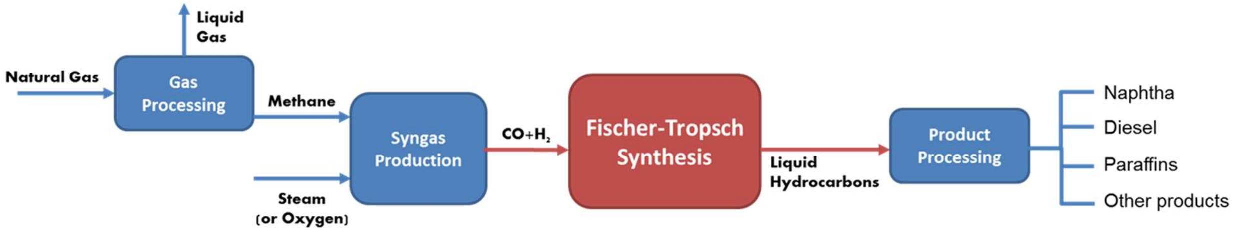

Figure 1 - Schematic of the GTL process.

two types of commercial reactors: slurry bubble column (SBCR) and multi-tubular fixed-bed reactors (MTFBR). These reactors are depicted in Figure 2. The reaction is highly exothermic and heat removal presents one of the main challenges when choosing the reactor type. However, other issues that also have to be considered are catalyst effectiveness, catalyst deactivation and regeneration, pressure drop etc. The differences between these reactor types have already been discussed elsewhere.[10-12] The major downsides of SBCR are difficult scale-up, separation of active catalysts from wax and catalyst deactivation due to attrition, while the drawbacks of MTFBR are high capital cost, poor heat removal, high mass transfer resistances and high pressure drop.[13] Some of these issues can be solved, or at least minimized, using the principles of process intensification.[14]

The GTL and CTL plants require very high capital investments (on the order of billions of US dollars) and the plant capacity necessary to recover capital cost over a plant lifetime and ensure profitable operation is above 30 000 bbl/day. This is why these plants can be placed only in locations with sufficient natural gas or coal reserves. Process intensification aims at reducing the size of the plant, and by doing that reducing the capital cost, while maintaining the economic viability.[15] In this way plant capacity can also be drastically reduced, enabling the utilization of smaller gas fields, as well as unconventional gas reserves. In addition, the process intensification also improves attractiveness of FTS for conversion of ligninocellulosic biomass into synthetic fuels using BTL technology. The efficiency of the BTL process is strongly affected by the cost related to biomass collection and transport.[3, 5] Design of smaller highly efficient BTL units is expected to significantly improve the cost-efficiency.

The design and construction of this new generation of smaller XTL plants was pioneered by Velocys Inc. Their technology is based on the use of coated microchannel reactors with “super active” cobalt-based catalyst.[16] Similar concept is offered by Compact GTL.[17] These reactors are characterized by high productivity per reactor volume, which is a general characteristic of novel microreactor technologies.

In this review the focus is on exploring options for intensification of FTS via reduced methane production on cobalt-based catalysts, i.e. improved yield of desired products. This can be achieved through better understanding of methane formation kinetics and development of guidelines for selection of optimal catalysts, process conditions and reactor configurations.

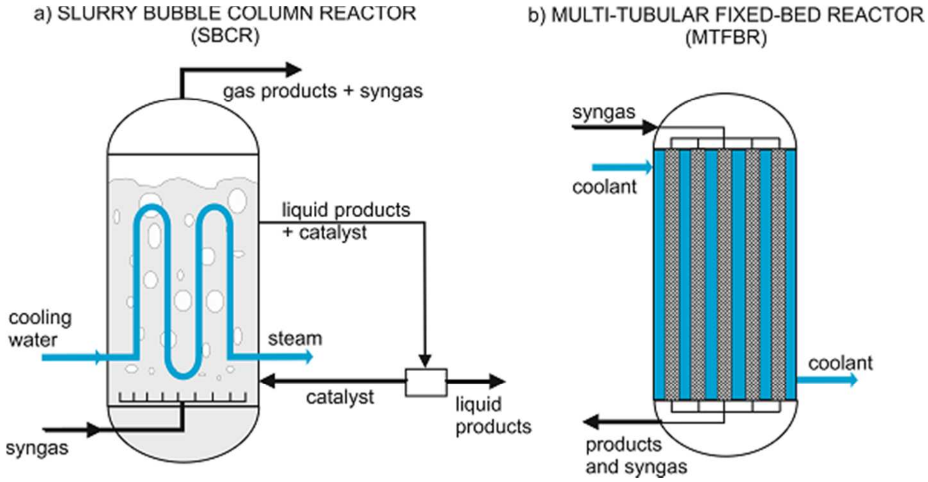

Figure 2 - Commercially used industrial reactors for low temperature FTS: a) slurry bubble column reactor; b) multi-tubular fixed-bed reactor

FTS product selectivity

FTS is a “non-trivial surface polymerization reaction”[18] and its selectivity is typically described using the Anderson-Schulz-Flory (ASF) distribution model. This model is characterized by a single parameter, i.e. the chain growth probability factor α. The ASF equation in terms of carbon selectivity is:

$$S_n = n \cdot (1-\alpha)^2 \cdot \alpha^{n-1} \cdot 100\% \qquad (2)$$

where S_n is the fraction of carbon atoms contained within chains with n carbons, i.e. the selectivity on carbon basis.[19] Equivalent equation can be derived in terms of hydrocarbon molar fractions.[20] According to the ASF model, logarithm of selectivity (or molar fraction) vs. carbon number should form a straight line, the slope of which is determined by the α-value (Figure 3).

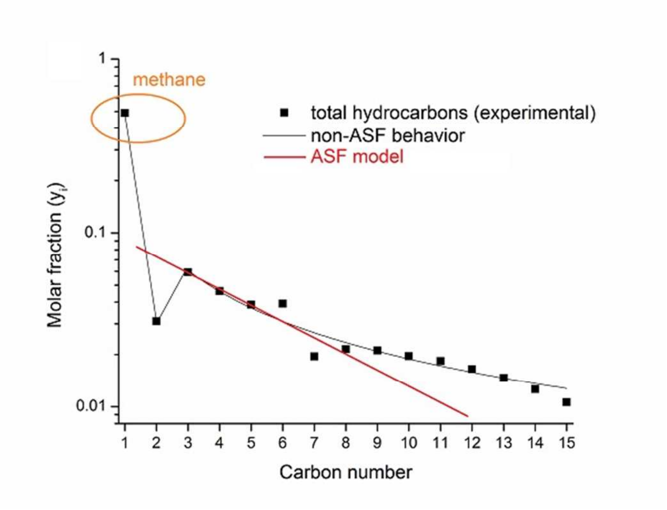

Figure 3 - Typical FTS product distribution over cobalt-based catalyst.

However, it is well known that the FTS carbon number selectivity does not fully obey the ASF model and three types of deviations have been observed: higher-than-expected methane yield, lower-than-expected ethene and higher selectivity towards heavier products due to increase in the α-value with carbon number[20-25] (see Figure 3). Out of these, the first and the last have the highest practical importance, since they represent the undesired and desired products of FTS, respectively. The focus of research efforts in the last twenty five years has largely been on determining the reasons for increase in heavy products with carbon number. A number of explanations has been offered for this phenomena and there is no consensus regarding this issue.[19, 23, 24, 26-30] In this work the focus is on reasons for methane deviation from the ASF distribution and their impact on the overall FTS selectivity.

The selectivity of FTS changes with process conditions. This is especially true for cobalt-based catalysts. The two most important selectivity aspects are selectivity towards methane and C_{5+}, i.e. selectivity to undesired and desired products, respectively. The dependence of these selectivities on process conditions has been well established.[31-34] It is known that CH_4 selectivity increases and C_{5+} selectivity decreases with increasing temperature and feed H_2/CO ratio, while increases in pressure and conversion level (up to about 80%)[35] may have the opposite effect.[31, 33, 36-39] However, the reasons for these observations are not entirely clear. An often mentioned reason for this type of selectivity behavior is the readsorption and continued chain growth of initially formed 1-olefin molecules.[40] This concept offers an elegant explanation for the variation of α-value with carbon number, as well as variation of selectivity with process conditions. Some researchers, however, critically question the importance of secondary reactions of 1-olefins.[27, 29, 41-45]

An alternative view on the selectivity changes was offered by Lögdberg et al.,[46] who analyzed variations of α-value with carbon number and showed that increase in C_{5+} selectivity is correlated with increase in the chain growth probability of C_1 intermediate (α_1). α_1 was defined in this study as chain growth probability of C_1 intermediate while α_n is the probability that the intermediate chain with n C-atoms will grow to the intermediates with n+1 C-atoms. This showed that the reason for at least some of changes in selectivity is the abnormal formation of methane, a largely unexplored area in FTS. A recent study from our group examined the effect of process conditions on a lab-scale FTS slurry reactor product formation kinetics over rhenium promoted cobalt catalyst.[20] The results confirmed Lögdberg et al. conclusion that C_{5+} selectivity is mainly determined by α_1 (Figure 4a). Also it was found that variations in process conditions (temperature, pressure, reactant feed ratio and conversion level) mainly affect the value of α_1, while α-values of C_2-C_4 hydrocarbons are relatively constant (Figure 4b). If secondary 1-olefin readsorption and continued chain growth played a major role in determining C_{5+} selectivity, one would expect to see an increase in C_2-C_4 growth probabilities with increase in residence time (i.e. conversion level in Figure 4b). The constant value of α_2 to α_4 implies that these reactions likely play only a minor role in determining product selectivity, and that variation of methane formation with process conditions is the key to obtaining higher selectivity towards C_{5+} products.

A typical value for α on a cobalt-based catalyst under standard FTS conditions is around 0.9. According to Eq. (2) if α = 0.9 then the methane selectivity should be about 1%. However, typical methane selectivity observed in experiments is between 3 and 10%,[20] i.e. it is several times higher than expected from the ASF model. Therefore it would be beneficial from a commercial, as well as scientific viewpoint, to take a closer look at methane formation in FTS and search for ways to reduce it. As shown above (Figure 4), this could have positive implications on selectivity of desired C_{5+} products.

Higher-than-expected methane formation in FTS over cobalt-based catalysts

Higher-than-expected methane formation in FTS on cobalt catalysts can be due to the mechanistic and kinetic reasons, reactor, reaction and process conditions. Several concepts explaining non-ASF behavior of methane have been proposed and include: high surface mobility of methane precursor,[47] hydrogenolysis of higher hydrocarbons by successive demethylation,[23] lower activation energy for methane formation compared to other products,[30, 48] and existence of different pathways for methanation reaction.[49, 50] A recent review of Yang et al.[51] discusses some of these concepts and offers an in depth review of the effect of CO conversion level on methane selectivity over various FTS catalyst. Perhaps the most accepted kinetic explanation for high methane is the existence of two different sites, i.e. FTS active sites and specific sites for methanation, or different reaction pathways.[52-54] According to Schulz,[52] the methanation reaction is mainly happening on active sites with different coordination than that of FTS active sites. Lee and Bartholomew[53] showed that support could play a role, where spillover CO and H species could react to form CH_xO complex, which then diffuses to FTS active metal sites and produces methane through decomposition. According to their study, increase in catalyst loading lead to a decrease in this secondary methanation reaction and favoring of FTS pathway. Further evidence for the hypothesis of separate methanation pathway is given by addition of water and ammonia, which both seem to inhibit secondary methane formation.[55, 56] Similar behavior is observed for 1-olefin hydrogenation and isomerization, which are also believed to happen on a secondary type of active sites.[52, 57]

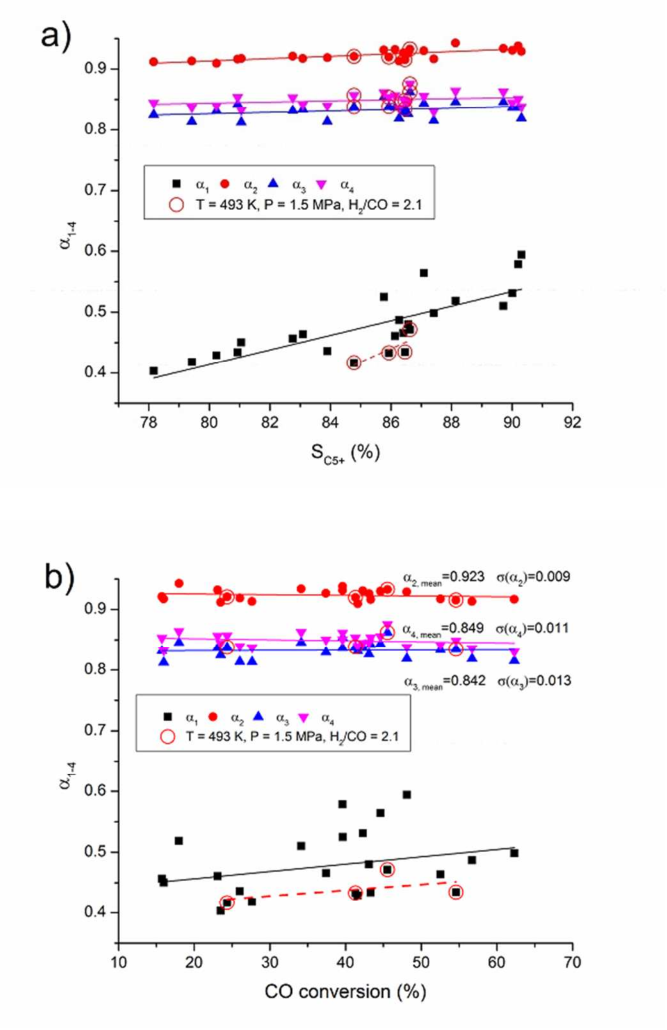

Figure 4 - a) Correlation between C_1-C_4 chain growth probabilities and C_{5+} selectivity; b) Variation of C_1-C_4 chain growth probabilities with residence time (conversion level). (*Note: Temperature, pressure and reactant feed ratio are varied.) (Reprinted from Ref. [20] with permission from Elsevier)

The effect of water on FTS with cobalt catalyst is somewhat controversial and conflicting results have been reported.[37, 58-61] Even though all studies seem to agree that addition of small amounts of water causes reduction in methane selectivity, its effect on reaction rate and catalyst deactivation are not fully understood.[37, 58, 62] High partial pressure of water is known to irreversibly deactivate cobalt based catalysts[63] and leads to increased methane selectivity,[35] most likely due to formation of methanation sites.[46, 52] If water is added in smaller amounts (less than ~ 20 vol% in the feed) this can either increase or decrease the rate of FTS, depending on the catalyst support, promoters, loading etc.[58] Water is believed to have a positive effect on rate through: better reactant diffusion in water,[64] removal of carbon species from the surface[65] and intrinsic kinetic effects.[66, 67] Higher-than-expected methane selectivity can be also attributed to partial cobalt oxidation which may occur in the presence of water at higher carbon monoxide conversions. Ma et al.[68] observed a considerable increase in methane and CO_2 selectivity on Ru-promoted Co/Al_2O_3 catalyst at high CO conversion. Much higher methane selectivity was also reported by Azzam et al.[69] in KL zeolite. The increase in methane selectivity coincided with oxidation of small cobalt particles. It was suggested that at higher CO conversion levels, additional hydrogen could be produced via water gas shift reaction catalyzed by cobalt oxides. The higher methane selectivity was attributed to higher H_2/CO ratio in the catalyst bed due to this side reaction.

Ammonia addition also reduces FTS catalyst activity. Recently, Pendyala et al.[56] reported that high concentrations of ammonia reduce methane selectivity and enhance the C_{5+} yield over a cobalt-alumina catalyst. Addition of both water and ammonia also results in higher 1-olefin selectivity.[56, 57] The proposed explanation is that these molecules block catalytic sites for hydrogen adsorption thereby reducing hydrogenation activity. Alternatively, the adsorption of water and ammonia onto sites on which secondary methane formation and 1-olefin reactions (hydrogenation and isomerization) occur could also explain the observed trends in selectivity.

Cobalt catalyst properties (such as particle size, phase and addition of promoters) have been shown to affect methane selectivity. The cobalt particle size does not affect the intrinsic catalyst activity (turn over frequency, TOF) in the ~10 to 200 nm range, as well as methane selectivity, however below 10 nm TOF decreases and methane selectivity increases.[7, 40, 70, 71] This difference between smaller (bellow ~10 nm) and larger (10 to 200 nm) cobalt particles was related to surface coverage of CO, H and CH_x. As measured by SSITKA (Steady State Isotopic Transient Kinetic Analysis) smaller particles had increased coverage of atomic coverage hydrogen, while in the range above 10 nm those coverages did not change with particle size.[70] Different phases of cobalt crystals (hcp and fcc) also exhibit different behavior and hcp is generally believed to be favorable both in terms of TOF and selectivity.[72-75] The addition of noble metal promoters is well known to enhance the rate of FTS, and their effect on selectivity is believed to be positive.[9, 40] A recent study by Ma et al.[76] shows that noble metals could potentially be used to enhance selectivity as well. In this study rhenium was highlighted as the promoter that had the most positive effect on both catalyst activity and selectivity.

Methane selectivity in FTS can also be affected by phenomena that are not intrinsically kinetic, but depend on reactor configuration. This is related to mass and heat transport phenomena. Fixed-bed reactor configuration could be particularly affected by poor mass and especially heat transport, leading to increased methane selectivity. The influence of these phenomena directly affect the intrinsic kinetic features, e.g. poor heat removal causes high temperature, which in turn causes higher conversion with high partial pressure of water, which irreversibly deactivates the catalyst and increases methane selectivity. The heat and mass transfer limitations could also lead to modification of the catalyst structure. The heat transfer especially during the reactor start up could lead to the formation of hot spots and even reactor runaway, and thus accelerate cobalt sintering and oxidation. Chambrey et al.[13] intentionally exposed the alumina supported cobalt catalysts to 260° and 340°C to simulate modification of catalyst structure in hotspots. After returning to 220°C, the methane selectivity was noticeably increased.

Mass transfer limitations change concentrations of reactants in the vicinity of catalytic sites, thereby altering the kinetics which results in shifting from intrinsic to effective kinetic coefficients. The rates at which hydrogen and carbon-monoxide diffuse into the catalyst pellets are different, where the latter diffuses slower.[77, 78] Significant mass transfer resistance leads to surface saturation with hydrogen and a lack of carbon-monoxide (high effective H_2/CO ratio) which in turn results in poor performance in terms of methane and C_{5+} selectivity. Catalyst pellets with diameter smaller than 200 µm significantly minimize mass transfer resistance. However for pellet sizes typically used in industrial fixed-bed reactors (1 – 3 mm) considerable mass transfer limitations can be expected.[11, 22, 79] Conventional fixed-bed FTS reactors, with tube diameters typically above 2 cm, also often experience temperature gradients and hot spots due to poor heat removal. High temperature favors production of methane and other light products; and at very high temperatures catalyst is deactivated and methane becomes the main product.[63]

However, the occurrence of mass and heat transport limitations combined with undesirable alternations of catalyst structure and active phases can be minimized through the use of intensified reactor configurations, i.e. microreactors.

FTS microreactors

Microreactors, as the name suggests, represent the reactors with characteristic sizes (of tubes or channels) in the order of micrometers.[80, 81] They provide a significant reduction in reactor dimensions, compared to conventional reactors, allowing for a significant reduction in capital costs (Figure 5).

Microreactors for FTS have recently received a lot of attention from both academic and industrial research community.[82] They offer potential to minimize mass and heat transport resistances that are present in conventional fixed bed reactors and which lead to higher methane selectivity. Several types of microreactors are available for FTS (Figure 6), including: 1) reactors with microstructured catalyst (e.g. monoliths and foams); 2) coated microchannel reactors, in which catalyst is coated over the walls of microchannels; and 3) micro- and milli-fixed bed reactors, in which sufficiently small catalyst particles are loaded into the packed bed, allowing for micro-scale flow characteristics.

The principal advantage of microreactors is enhanced heat transfer which is often problematic in conventional centimetric fixed bed reactors. The temperature control can be particularly demanding during the reactor start up, when the uncontrollable temperature surge can affect the catalyst structure. Because of the enhanced heat transfer, more active catalysts with much higher hydrocarbon productivities can be used in the microreactors. One of the disadvantages associated with conventional reactors is the chaotic nature of fluid dynamics in the reactor, i.e. turbulent fluid flow between catalyst pellets within the fixed-bed or gas bubble and liquid phase behavior within the SBCR. Microstructured catalysts and reactors overcome this by having organized spatial structures, allowing for more regular fluid behavior (e.g. laminar flow) and thus better control of physical heat, mass and momentum transport phenomena.[83] Microstructured catalysts are formed by coating a structured support, such as honeycomb monolith, with a thin layer of catalyst. In this way the catalyst and reactor really become inseparable entities, since the structured catalyst is placed inside the reactor as a whole and not as the sum of individual catalyst pellets. A monolith catalyst consists of many parallel channels, which are separated by thin walls, coated with the active catalyst.[84] In this type of structure the heterogeneous gas-liquid mixture often follows the Taylor flow pattern.[85] Taylor flow is characterized by elongated gas bubbles, whose typical equivalent diameter is significantly larger than that of the channel diameter (Figure 6a). Gas bubbles are separated by the liquid phase flow. A very thin layer of liquid also separates the gas bubbles from the walls coated with the catalyst. This means that the reactant molecules from the gas phase will have to travel a very short distances to reach the active catalyst surface, which results in a very small mass transfer resistance. By analogy, this applies to heat transport resistance as well, i.e. heat is easily removed from the wall. It should be noted though, that experimental magnetic resonance imaging measurements of two-phase flow in different reaction environments conducted by Stitt and co-workers[86-88] showed that flow in monoliths deviates from ideal Taylor flow behavior. In addition, in order to achieve Taylor flow regime high liquid flow rates may be required and the use of liquid phase recycle is needed in a monolith loop reactor.[89, 90] The monolith structure offers a very high open cross-section area for fluid to flow through, resulting in a very low pressure drop. Similar values of heat and mass transport rates, albeit with somewhat higher pressure drops, can be achieved with other types of microstructured catalysts, such as foams, wires and fibers.[83] Flow in these structures is often approximated as plug flow, due to its turbulent nature.[91]

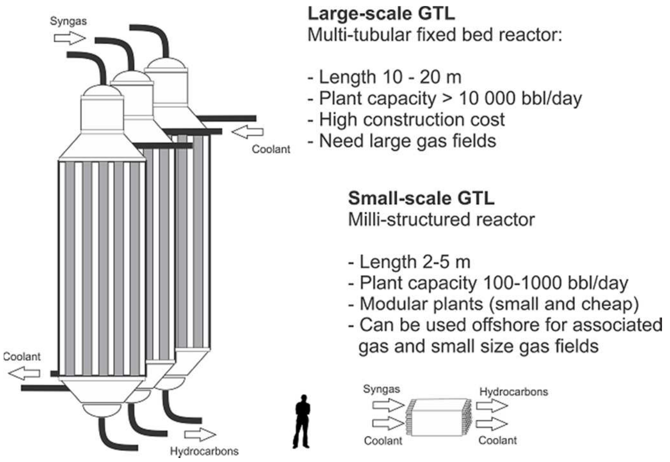

Figure 5 - Comparison of large-scale multi-tubular fixed bed and small-scale milli-structured FTS reactors.

Holmen and co-workers[90, 92, 93] used monolith, coated with Re-promoted Co/Al_2O_3 catalyst, for FTS applications. Their results showed that methane and C_{5+} selectivity, as well as olefin/paraffin ratios, depended on the coat loading, i.e. thickness of coated catalyst layer, due to the occurrence of transport limitations. However, both activity and selectivity of cordierite monoliths, with catalyst layer thickness of 40 – 50 µm, was comparable to a classical powder catalyst (< 90 µm).[92] Hilmen et al.[92] showed that methane and C_{5+} selectivities are 8.9 and 82.5%, respectively, for monolithic cobalt catalyst with layer thickness of 40 µm, compared to 8.3 and 82.3% for powder catalyst used in a slurry reactor. Almeida et al.[94] showed that increasing catalyst loading from 255 to 908 mg (i.e. increasing coating layer thickness) caused increase in methane selectivity from 20.8 to 27.1% for monoliths, even though the overall CO conversion increased from 19.2 to 58.2%. Using the Krishna and Sie[95] approach for multiphase reactor selection, de Deugd et al.[82] analyzed several reactor types and found the monolithic reactor to be especially fitting for FTS application. Several research groups used monolith catalysts for FTS in the past decade.[90, 92, 96-113] Kapteijn et al.[98]

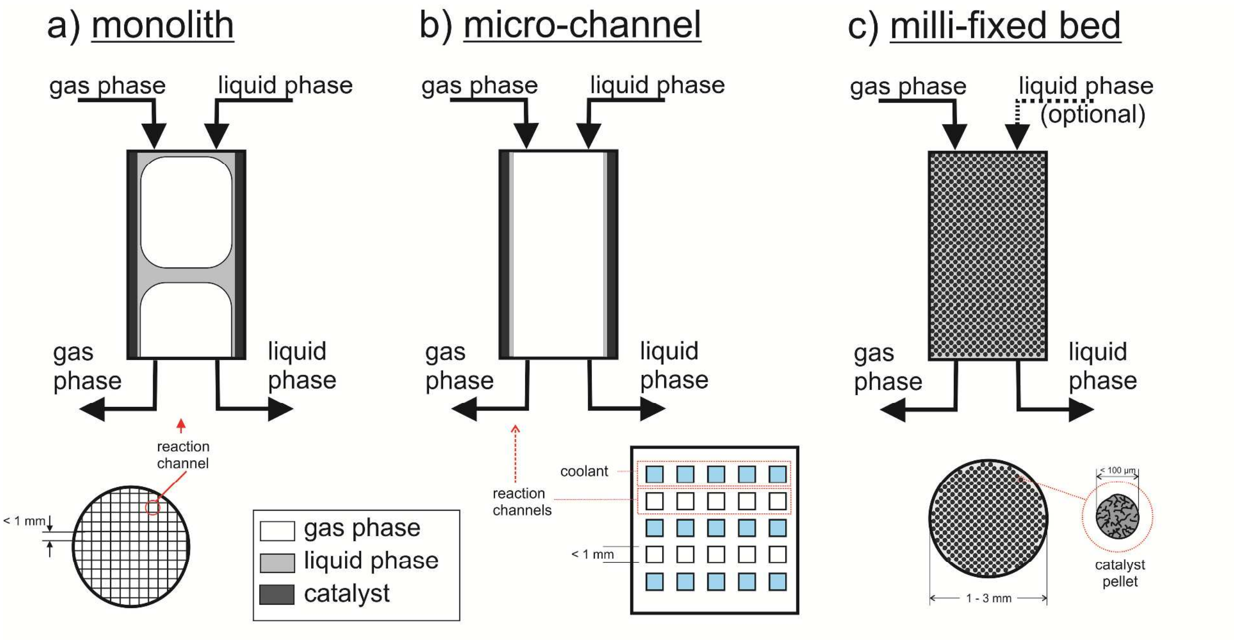

Figure 6 - Schematic representations of some microreactors for FTS (typical flow pattern and cross-sections): a) monolith microstructured catalyst reactor; b) microchannel reactor; c) milli-fixed bed reactor.

showed the effect of monolith catalyst washcoat layer thickness (from 20 to 100 µm) on FTS activity and selectivity. Similar to previous reports,[92,94] their results showed that the FTS activity and selectivity are intrinsically kinetic for layers up to 50 µm, while thicker layers exhibit clear signs of diffusion limitations. This study showed that activity and selectivity of FTS can therefore be tuned by optimizing the thickness of monolith catalyst washcoat layer.

Even though monolith support has been used most frequently for FTS applications, it has been shown that other structured catalyst supports (e.g. foam and wire) have similar performance characteristics.[91] It seems that performance of the structured catalysts is similar to, or in some cases even better, that of conventional catalysts in terms of activity and selectivity. However, the biggest drawback of structured catalysts is their lower volume-based activity. In other words, these reactors hold smaller amount of active catalyst per reactor volume which limits their productivity. Most recently carbon nanofibers (CNF) have been proposed as a support for catalytic reactions and especially FTS in order to enhance the activity per reactor volume, due to their larger surface area.[102, 114, 115] However, these catalysts exhibited rapid deactivation at industrial FTS conditions.[115] This issue was addressed by Zhu et al.,[114] who applied Co catalyst on SiO_2 support coated on carbon nanofiber structure, using the sol-gel method. The application of uniformed SiO_2 layer increased the catalyst stability.

Another type of FTS microreactors are the microchannel reactors (Figure 6b). These reactors are very similar to monolith in their general design, with the main difference being in the way in which heat is removed and in flow patterns. The microchannel reactors have been studied by several research groups.[91, 101, 116] This technology has also been extensively used in industry.[117-119] Microchannel reactors consist of a large number of parallel rectangular channels, which are coated with a thin layer of active catalyst, most often sorted into blocks. Due to their high surface area-to-volume ratio, they offer high mass and heat transfer coefficients, several times larger compared to conventional reactor technologies.[120] This in turn enables operation at severe process conditions needed to achieve best activity and selectivity, such as increased temperature, conversion level and pressure. They differ from microstructured reactors in that coolant fluid flows through the parallel uncoated channel rows (Figure 6b). Unlike monoliths, fluid flow in these FTS reactors is typically laminar. This technology was initially employed for FTS by Velocys.[117-119] Velocys researchers[119] reported methane selectivity for these reactors at about 9%, which is similar to slurry phase experiments with powder catalysts and monoliths with thin catalyst layers.[94] Their fabrication is relatively simple and consists of stacking many thin sheets with solid walls one on top of another. This leads to cost effective manufacturing and robust design.[118] Guettel and Turek[89] compared conventional reactors (fixed-bed and slurry) with novel microchannel and monolith reactors using mathematical modeling. Their analysis focused on reactor effectiveness and effect of mass and heat transfer on effectiveness. Simulation results showed that slurry reactors exhibit a ten-fold higher effectiveness compared to fixed-bed and require both less active catalyst mass and reactor volume, due to better mass transfer characteristics and isothermal operation. Monolith catalyst reactor exhibited a similar yield-to-reactor volume compared to fixed-bed reactor, but no heat transfer issues. However, both slurry bubble column and monolith reactor suffer from practical issues; removal of catalyst particles from liquid products in the slurry reactor and high liquid recycle flow rate needed in monolith reactor for heat removal. On the other side, Guettel and Turek[89] showed that microchannel reactors do not have such issues and exhibit very high reactor efficiency, due to negligible heat and mass transfer resistances. However, the very low catalyst mass-to-reactor volume ratio meant that their productivity per reactor volume (with conventional catalysts) is not high enough for industrial application. Their application is possible with the new generation of highly active catalysts, developed by the Oxford Catalyst Group[121]. Such microchannel reactors with highly active catalyst are already being tested on industrial scale by Velocys plc. (merger of Oxford Catalysts Group and former Velocys Inc.).

Almeida et al.[91,94] studied the performance of different structured catalysts (monolith, micromonolith and foam), comparing them to powder catalyst and microchannel block reactors. They found that microchannel reactors had similar or better performance compared to structured catalysts, in terms of catalyst effectiveness and methane and C_{5+} selectivity, at similar process conditions. Their results showed that microchannel reactors had methane selectivity ranging from 5.0 to 18.1%, depending on the loading, while monoliths and foams typically exhibited methane selectivity of ~ 20%.[94] Recently, Holmen et al.[101] reviewed and compared different microreactor types used by their group in previous studies (monolith, carbon nanofibers and microchannel reactors). The results for these reactor types show comparable CO consumption and hydrocarbon formation rates. The microchannel reactor showed the highest reaction rates on the basis of cobalt and catalyst masses, but was outperformed by microstructured carbon nanofiber catalyst in terms of CO conversion per reactor volume. They also point out that monoliths and carbon fiber structured catalysts *"are relatively easy to handle (shape to any type) and can be used in fixed-bed reactors directly"*, while microchannel reactors *"need to a larger extent to be designed and fabricated to the purpose, but they offer possible advantages in terms of control and safe operation of the vessel, if the parallelized/compartmented approach is maintained throughout"*.

The most significant downside of the coated FTS microreactors (microchannel and structured catalyst reactors) is the above mentioned low catalyst mass to reactor volume ratio, resulting in low hydrocarbon yield. However, others disadvantages exist, such as difficult reactor wall coating procedures and the need for specially designed catalysts for coating.[13] This is why some authors have looked into the possibility of using micro- and milli-fixed bed reactors (Figure 6c), in order to reap the mass and heat transport benefits of microreactors, while retaining high catalyst mass to reactor volume of the fixed bed reactor.[13, 122] Additional advantages of such configurations are the ability to use "tried and proven" catalysts, easy reactor loading and possibility of catalyst replacement.[13] As expected, the main issue with these reactors is a very high pressure drop, due to the use of very small catalyst pellets. However, Knochen et al.[122] showed that the acceptable pressure drop can achieved with catalyst pellets as small as 100 μm, while maintaining high catalyst effectiveness. They also showed that tubes as large as 3 mm can be utilized to benefit from the intensified high heat transfer on the micro-scale. Therefore, this type of configuration also displays much better control and deactivation characteristics compared to conventional reactors and can be considered for future application.

Recommendations for intensification of FTS in terms of selectivity

Based on analysis of our experimental results, obtained under a range of typical FTS conditions, it seems that one of the best ways to improve FTS selectivity could be to reduce excess methane formation.[20] This can be done in several ways, i.e. by optimizing the catalyst, as well as the process conditions within the reactor and within the catalyst pellets.

First, better understanding of intrinsic methane formation kinetics is needed. As pointed out before, methane deviates from the ASF FTS kinetics most likely because of the existence of several formation pathways. One experimental method that could help elucidate methane kinetics is the Steady-State Isotopic Transient Kinetic Analysis (SSITKA). In this technique, one of the reactants is abruptly replaced by its labeled isotope. For SSITKA application in FTS, usually labeled ^{13}CO is used, since D_2 exhibits isotopic effects.[123] There have been several investigations in which SSITKA was used to study the FTS reaction mechanism.[49, 70, 123, 124] It is interesting however that SSITKA studies are typically performed at conditions favoring methane formation, i.e. high temperature, low pressure and high H_2/CO ratios. Therefore, extrapolation of SSITKA results in the analysis of overall FTS kinetics (as done so far) is questionable, since it is based on analyzing methane formation, which deviates from overall FTS ASF distribution. However, its application in analyzing the kinetics of methane formation kinetics within FTS is undoubtedly justified. To our knowledge, this type of study was only performed by Govender et al.[125] They proposed a mechanistic kinetic model for methane formation over Fe-based catalysts, consisting of two parallel methane formation pathways. This is something that requires further consideration and such detailed kinetic models of methane formations should be investigated for Co-based FTS catalysts as well.

Having reliable FTS methane formation kinetic models would help analyze the effect of process conditions on methane selectivity and reduce the selectivity towards this undesired product by selecting the optimal set of conditions.

Second important implication of this viewpoint is that one could conceivably control the methanation rate through catalyst design by shutting down the additional methanation pathways.[20] An ideal catalyst would produce methane only through FTS reaction (i.e. have CH_4 selectivity close to 1%). Methane selectivity could therefore be reduced by optimizing the size of cobalt catalyst nano-sized crystals,[71] extent of reduction, metallic cobalt phase composition and support structure,[75] as well as selection of optimal catalyst loading[53] and catalytic promoters.[76]

Third improvement in methane selectivity, and FTS intensification as a whole, is the use of knowledge of methane formation kinetics in the reactor design. As described above, heat and mass transfer resistances play a significant role in determining methane and C_{5+} products selectivity, since the temperature and concentrations of reactants near the active catalyst sites are often very different from those inside the reactor fluid bulk. By applying new microreactor concepts, with intensified mass transfer, these temperature and concentration gradients can be minimized. Some characteristics of different FTS microreactor types are summarized in Table 1. The use of such reactors would also benefit from improved heat transfer, enabling better temperature control which in turn would result in lower catalyst deactivation and more stable product distribution over time.

Table 1 - Comparison of main characteristics of microreactors (data from Refs. 92, 112, 118).

Characteristic		Monolith	Micro-channel	Micro fixed-bed
Surface area	Rank	2	3	1
	m^2/g	160	N/A	184
Porosity	Rank	2	1	3
	%	89	N/A	<70
Heat transfer	Rank	2	1	3
	W/cm^2	N/A	1-20	~ 1
Mass transfer	Rank	2	1	3
Pressure drop	Rank	2	1	3
Catalyst loading	Rank	2	3	1

Conclusions

FTS is an important part of XTL technology which monetizes vast resources of natural, shale gases, coal and biomass by converting them into value-added liquid hydrocarbon fuels and chemicals. Methane is an undesirable product of this reaction and its formation during FTS leads to major carbon losses in the XTL technology. The available literature data suggest that the catalytic performance of cobalt FT catalysts and methane selectivity depend on catalyst, reaction conditions and reactor configuration. This also suggests possible ways for improving long-chain hydrocarbon productivity and reducing methane formation.

Methane selectivity could be reduced by optimizing the size of supported cobalt nanoparticles, cobalt reducibility, metallic cobalt phase composition, and support porous structure. It could also be reduced through optimization of reaction conditions (reactant partial pressures, conversion level, addition of water etc).

Methane selectivity especially in conventional centimetric fixed-bed reactor is affected by both heat and transfer phenomena. Higher methane selectivity in packed beds is due to severe intraparticle diffusion limitations. Insufficient heat transfer also results in higher methane selectivity and leads to accelerated catalyst deactivation. Microreactors with enhanced mass, heat transfers and excellent mixing could potentially reduce methane formation in FTS. However, this potential has not been fully materialized yet.

It is important to gain better understanding of intrinsic methane kinetics and develop kinetic models for more reliable prediction of methane formation. Such knowledge combined with optimized catalyst design and modeling of reactor hydrodynamics and mass transfer would provide opportunities to greatly improve the productivity of FTS and to reduce undesirable methane formation.

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Notes and references

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