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Abstract: Synthesis gas production and further conversion via the Fischer-Tropsch, methanol and dimethyl ether (DME) syntheses is currently economic only in the large scale. Compact, modular, and safe technology efficient in smaller scale would enable utilizing smaller natural gas fields, bio-syngas and even off-shore associated gas that otherwise would be flared or re-injected. So-called or microstructured reactors with superior heat and mass transfer properties and scalability by parallelization may offer opportunity for process intensification and different investment risk. Here, we summarize research into the performance of different combinations of catalyst properties and microchannel design.

We find that intensified production of synthesis gas by steam reforming or catalytic partial oxidation remains associated with significant challenges to the reactor design, the catalysis and the materials. With respect to synthesis of methanol, DME or Fischer-Tropsch products, using a microchannel packed-bed with integrated heat exchange, the results are definitely more encouraging, enabling the use of highly active catalysts and severe process conditions without sacrificing on selectivity and stability.

## Highlights

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Catalysis in microstructured reactors – short review on small-scale syngas production and further conversion into methanol, DME and Fischer-Tropsch products

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- Research on catalysis in microreactors for synthesis gas production and conversion has been reviewed
- Small-scale syngas production remains challenging (POX, SMR), especially materials stability
- MeOH, DME and FTS: Isothermal, isobaric reaction environment free from mass transfer limitations
- Enables use of high-activity catalyst beds and high conversion levels; catalyst stability maintained

# **Catalysis in microstructured reactors – short review on small-scale syngas production and further conversion into methanol, DME and Fischer-Tropsch products**

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## **Abstract**

Synthesis gas production and further conversion via the Fischer-Tropsch, methanol and dimethyl ether (DME) syntheses is currently economic only in the large scale. Compact, modular, and safe technology efficient in smaller scale would enable utilizing smaller natural gas fields, bio-syngas and even off-shore associated gas that otherwise would be flared or re-injected. So-called or microstructured reactors with superior heat and mass transfer properties and scalability by parallelization may offer opportunity for process intensification and different investment risk. Here, we summarize research into the performance of different combinations of catalyst properties and microchannel design.

We find that intensified production of synthesis gas by steam reforming or catalytic partial oxidation remains associated with significant challenges to the reactor design, the catalysis and the materials. With respect to synthesis of methanol, DME or Fischer-Tropsch products,

using a microchannel packed-bed with integrated heat exchange, the results are definitely more encouraging, enabling the use of highly active catalysts and severe process conditions without sacrificing on selectivity and stability.

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## 1. Introduction

Natural gas, biomass and coal may be converted to fuels and bulk chemicals, i.e. Fischer-Tropsch synthesis (FTS) products, methanol and/or DME, hydrogen, and ammonia, via synthesis gas generated by feedstock dependent combinations of (steam/dry) reforming, (partial) oxidation, and gasification reactions [1, 2]. Syngas is a mixture of CO and hydrogen which depending on the end product may also contain N<sub>2</sub>, H<sub>2</sub>O or CO<sub>2</sub>, as well as trace amounts of inerts (e.g. Ar) or impurities originating from the specific feedstock (S and N compounds, alkali metals). Some general features of these routes are use of several catalytic steps, strong requirements on energy integration, and - importantly – all commercial technologies have strong scale-dependent economic characteristics [2-5]. The Pearl GTL plant operated by Shell and Qatar Petroleum and producing 140,000 barrels of GTL products per day may be considered the most prominent example of this, with its 28,800 tons per day oxygen separation plant, 18 partial oxidation reactors, and 24 FTS tubular fixed bed reactors with integrated heat exchange containing altogether several thousand tons of catalyst. There are several drivers that make industries and researchers pursue alternative technologies that challenge these dependencies of scale [6]:

- a. Large scale means large investments and long time horizon. This adds to the investment risk to the extent that decisions on plant development become extremely difficult. Several announced, but then terminated or halted, FTS based developments are testimony to this. Enabling a stepwise construction and commissioning of efficient process plants would radically change the economic perspective.
- b. Several natural gas fields are smaller and must be developed in a smaller scale. There is also gas associated with oil, which should find a way to the market rather than being flared, injected or – even worse in a global warming perspective – vented [7]

- c. With respect to biomass gasification for syngas production, the scale limit is given by the optimization of feedstock harvesting. It has been estimated that one ton of biomass is needed for producing one barrel of fuel, hence there will be a limit to how far the biomass should be transported for the conversion to be meaningful.
- d. Related to b. and c. above is the location of the process, which may have other requirements with respect to safety, security and environmental hazard than a relatively remote, land-based field development.
- e. Small scale production of hydrogen pursued as a possible enabler of a future fuel cell and hydrogen based society [8-10]. However, car manufacturers have mostly abandoned fossil-to-hydrogen routes that do not involve CO<sub>2</sub> capture and storage (CCS), in recognition of the need to abate climate change in future energy systems. This links production of hydrogen as an energy carrier mainly to large scale, but specific cases may exist for e.g. bioethanol or diesel based auxiliary power units [11-13]

Different approaches thus exist to enable cheaper, safer and more efficient conversion of the fossil or renewable carbon based feedstock to the fuels and bulk chemicals required in the future. So-called microstructured or microchannel reactors (also referred to as microreactors), exhibiting radically enhanced heat and mass transfer in combination with highly active, selective and stable catalysts, are part of such process intensification. The microstructured reactors may be defined as reactors with characteristic dimensions in the micrometer range (1-1000 $\mu$ m) [14, 15]. This gives different intrinsic properties as compared to larger reactor volumes. And since the scale-up to commercial production is intended to happen by parallelization, the properties are maintained or transferred to the larger scale, leading also to new challenges. Such reactor technology has been developed mainly over the recent 20 years, with a few research environments as pioneers; the German Forschungszentrum Karlsruhe (now Karlsruhe Institute of Technology) [16-20] and Institut für Mikrotechnik Mainz (now

Fraunhofer ICT-IMM) [9, 10, 15, 21], and the US Pacific Northwest National Laboratory (PNNL-Battelle) [22] among the most active. The microstructured reactors' properties and potential have also been extensively reviewed and analyzed [15, 23, 24]. Reactor systems realized mainly in glass and plastics are now practically “off-the-shelf”, or -alternatively – available as 3D-printing technologies. This has enabled realization of the potential in the fine chemical industry, leading to better yields and selectivity, less by-product and waste, change from batch to continuous operation, and even completely new routes and chemistries [23, 25].

With respect to syngas conversion to fuels and bulk chemicals, industrial roll-out remains to be seen, but the commercialization efforts have been considerable. A few research groups and companies have led the way in this. Velocys was formed in 2001 on basis of research at the PNNL-Battelle, and later merged with Oxford Catalysts [22]. CompactGTL was formed in 2006 out of results from the UK Atomic Energy Authority R&D programme at Harwell [7]. Petrobras has been particularly active with respect to launching pilot/demonstration projects in alliances with the developers, and seems to have had both biomass and offshore associated gas conversion in mind [7]. A short list of features that may be considered as essential to process intensification of synthesis gas production and conversion may be given as:

- The small dimensions generally lead to large gradients in temperature and concentration, large surface area per volume, and hence efficient mass and heat transfer.
- The flow of gas (or liquid) can be controlled, and will often be laminar with possibility of limiting the flow dispersion, hence narrowing the residence time distribution. In two-phase systems, the liquid gas contact can be controlled to high precision.
- Inside the small volumes, gas phase reactions may also be affected, thus different interplay between homogeneous and heterogeneous chemistry.

- The geometry can be – if necessary/beneficial - optimized for the process in question, for example by enabling precise mixing or distributed dosing of one reactant, or for complete utilization of expensive catalysts.

Microstructured reactors for thermochemical conversion are restricted mainly to metallic and ceramic materials, and the fabrication methods follow thereof; different varieties of precision casting, machining, etching, welding and bonding techniques [14, 15]. Most common is the use of ferrous alloys or similar materials that tolerate high temperature and enable heat exchange and facile interconnections with tubing, etc. A common methodology for microchannel fabrication is known as lamination, producing many parallel channels by stacking and consolidating (bonding) thin sheets of material (laminae or shims) with microchannel patterns [26]. This technique seems to allow some cost effectiveness, design flexibility and sufficiently uniform internal passages.

The catalysts used for the microchannel reactor can either be as a coating on the inner wall of the microchannels or as loose particles (“powder”). A more rare case is also realizing the complete reaction geometry in the catalytically active material, e.g. Rh [19], Cu or Ag [27]. The advantage of a coating is that high space velocity can be used without significant pressure drop. The disadvantage may be relatively low productivity due to limitations in the amount of active catalytic material. It hence possibly best suited for high temperature, short residence time reaction systems. In addition, and depending on the system, homogeneous catalyst loading and refurbishment could be problematic. Powdered catalysts, on the other hand, are easier to load and exchange and existing (commercial) catalysts can be directly



used. The limitation is that high pressure drop may occur if too small particles are used, or if the superficial gas velocity becomes high.

At the Norwegian University of Science and Technology (NTNU) we have since ~15 years worked jointly with SINTEF and KIT to explore the potential and challenges associated by catalysis in microchannel reactors, with particular focus on natural gas conversion and building on research and competence developed in collaboration with Norwegian and international industry [28-45]. This paper is intended as a mini review and summary of our findings that – supplemented by relevant or preceding work of others – points to further opportunities as well as the limitations that have emerged. A few recent results have also been included. Related research topics or alternative approaches that will not be further addressed here include the effort to convert CH<sub>4</sub> directly to products such as olefins and aromatics [46, 47] and the direct thermochemical transformation of (lignocellulosic) biomass to suitable platform chemicals [48, 49]. The development of alternative separation technology based on membranes is considered interesting not only with respect to efficiency and scalability, but also in view of the potential of beneficial integration with the reaction [45-48].

## **2. Synthesis gas and hydrogen**

Syngas is conventionally produced by reacting (preconditioned) methane (or higher hydrocarbons) with steam, CO<sub>2</sub> and/or oxygen at high temperature [1-3]. Steam or dry reforming (SMR, DMR) alone is always catalytic, whereas partial oxidation (POX) and autothermal reforming (ATR) reactors may be completely or partly homogeneous. The process layout is adapted to the desired synthesis gas composition and process conditions of the subsequent syngas conversion step, and combinations of the abovementioned reaction schemes may be applied to achieve this. The reactor designs are given by the heat

requirement of the reaction schemes applied, with a high heating requirement for the endothermic SMR/DMR and high temperature tolerance needed for the POX/ATR reactors. Challenges that follow are related to heat transfer and carbon formation in the catalytic bed, as well as a range of material integrity issues [2, 50, 51].

Knowing these challenges to existing technology, it was realized that microstructured reactors could potentially lead to significant process intensification by clever heat transfer designs [10, 52, 53]. A good example is the calculations by Velocys and others on the potential for SMR intensification by efficient heat exchange by heating channels for catalytic combustion integrated between reaction channels and catalyst utilization. A microchannel heat-exchange SMR reactor was, using known characteristics for materials and catalysts, estimated at 1/10 of the size of a conventional steam reformer of equivalent capacity [54]. Nevertheless, and despite the many efforts worldwide, such heat exchange SMR reactors have proved to be difficult to realize commercially. The reasons for this have been little discussed in the open literature.

Current challenges with catalyst (and material) stability for SMR in microreactors, carbon formation in particular, result in a lower limit of the steam-to-carbon ratio (S/C) that may be as high as 4-5. This again gives too high  $H_2/CO$  for downstream conversion to methanol, DME or Fischer-Tropsch products. At best, the unconverted, excess  $H_2$  could be purged and used for e.g. heat generation. But in reality it introduces complications due to the thermodynamics and kinetics of the syngas conversion, generally reducing conversion and/or selectivity and possibly even affecting the stability of the catalyst by changing its chemical state. New or improved catalysts may hence be beneficial to fully take advantage of the heat

transfer efficiency, and several approaches exist to obtain active, thermally stable steam reforming catalysts with low carbon formation potential [55]. Issues related to carbon formation on the catalyst may furthermore have additional consequences in the case of microchannels. Given the improved heat transfer, hot spots may be less of an issue - but plugging definitely would be. Nevertheless, the designs should enable a more precise control of the reaction environment, temperature in particular.

In terms of catalytic partial oxidation, one idea was that the use of e.g. metallic microchannel monoliths could potentially suppress the strong thermal gradients by heat dissipation in the material and transfer by convection as compared to e.g. ceramic monolith and foam short contact time systems pioneered by Prof L. Schmidt and co-workers [56-58]. The microchannel reactors adopted in our studies were fabricated by the Institute of Micro Process Engineering (IMVT) at Karlsruhe Institute of Technology (KIT), in Germany, and the details have been described previously [28-31]. These were produced from stacked, micromachined foils (Fecralloy, Rh, Nicrofer), diffusion bonded to create about 700 channels of 20 mm length and ~100  $\mu\text{m}$  width. A catalytic coating was created by heating the Fecralloy monoliths to very high temperature under air, to form an alumina layer that increased the total surface area by a factor of ~10 relative to the monoliths' geometric surface. In the case of the Nicrofer monolith, sol-gel coating was applied to create the alumina layer [31]. Catalyst, usually Rh [28-31] but also Ni [28], was impregnated onto the alumina surface layer inside the channels.

Using the prepared Rh/Al<sub>2</sub>O<sub>3</sub>/Fecralloy microchannel monoliths, we performed investigations without and with steam addition to propane/O<sub>2</sub>/N<sub>2</sub> mixtures of C/O in the range 0.5-0.8 [28-

31]. At the time, hydrogen production was targeted and oxidative steam reforming (OSR) was used to describe the case of steam addition, in order to distinguish our reactor from conventional ATR and since the overall heat balance was not focused in these particular lab experiments. Illustrations of the reactor geometry and appearance under reaction conditions are displayed in Figure 1, along with selected results.

It was found that the metallic microchannels indeed gave significantly smaller thermal gradients (Fig. 1b) than e.g. impregnated alumina foams [30]. Typically a gradient of 100K was measured at the highest temperature obtained before ignition of the gas phase in front of the monolith took place. The catalytic monoliths also appeared surprisingly stable over a large number of cycles in terms of activity, selectivity and reactor material integrity. The high conversion prevailing for oxidation reactions at high temperature makes it difficult to quantify deactivation by established methodology, but conversion in conjunction with unchanged H<sub>2</sub> and CO selectivity was interpreted as good catalyst stability since complete combustion or thermal cracking were not becoming increasingly influential [30]. In addition, we ultimately dissected used monoliths to establish that the alumina layer was mostly intact and Rh particles were present, albeit some structural change and sintering that may have occurred (Fig. 1e) [31]. The work also demonstrated that choice of alloy and method of alumina coating preparation is very important; the alloy Nicrofer coated by alumina (sol-gel) proved prone to deactivation by structural change and “burial” of the impregnated active element [31].

The final, and potentially the most notable result, may relate to the interplay between gas phase and surface reactions. Under the conditions applied, the molecular mean free path is

comparable to the relevant dimensions of the catalytic microchannels, hence free radical chain mechanisms should be prone to quenching. This was supported by our results (Fig. 1b-d), which displayed low levels of propane thermal cracking products until the catalyst ignited the gas phase in front of the catalyst at  $\sim 750^\circ\text{C}$  furnace temperature. Hence, a nearly complete suppression of gas phase chemistry may be possible by eliminating any larger volumes, but this will require careful design and substantially increase the complexity of some experiments.

Catalytic OSR/POX schemes allow syngas compositions closer to those required for methanol, DME, or FT synthesis. But the use of pure  $\text{O}_2$  as reactant is required, since  $\text{N}_2$  in the syngas is highly unfavorable due to cost and/or thermodynamic limitations. The previously mentioned oxygen membrane technology for  $\text{O}_2$  separation may hence be an enabler for small-scale syngas production. So-called Ion/Oxygen Transport Membrane (ITM/OTM) technology for  $\text{O}_2$  separation or integration with reaction, typically partial oxidation or oxidative steam reforming, has been under development during  $\sim 30$  years, with the pilot or (semi)commercial stages emerging. [59-61]. The membranes transport  $\text{O}^{2-}$  via lattice vacancies at high temperature; often with a secondary phase incorporated to transfer the electrons (net zero charge transport). The obstacles thus mainly have concerned these materials, i.e. ensuring the integrity of the mixed oxide under the more or less severe gradients across the membrane (C, P, T). In addition, carbon formation and catalyst stability issues are maintained or enhanced. Integration of membrane separation with the POX/OSR reaction in principle also lends itself favorably to microstructured reactors, since there appears to be good opportunity for optimization of catalyst activity to match the membrane mass (and heat) transfer.

Thermodynamic limitations may also be alleviated by e.g. extracting a product such as hydrogen. Thin Pd-alloy membranes are being developed for hydrogen separation from mixtures, and have been favorably integrated with methanol steam reforming, water gas shift and steam reforming [62]. Jointly with Bredesen et al. at SINTEF, we developed a microchannel membrane configuration for hydrogen generation and separation [63]. The specific Pd alloy membranes applied are prepared by magnetron sputtering to low thickness (1-10  $\mu\text{m}$ ), yet free from pinholes, and with the possibility of transfer to different geometries or supports [64]. So far, we applied the configuration mostly to investigate fundamental phenomena relevant to the membrane transport, such as mass transport [63], effects of co-reactants such as CO and CO<sub>2</sub> [65, 66], and structure effects on the hydrogen solubility and adsorption [67]. The integration Pd membranes with steam reforming directly is highly desirable, but still challenging due to the membranes' thermal stability at temperatures exceeding 500 °C [62]

One aspect that may have been initially underestimated is the consequence of the increased reactor surface area of microchannel reactor volumes. Metal dusting corrosion is a well-known phenomenon in conventional syngas technology that carries large costs and is so far only controlled rather than eliminated in commercial installations [68]. It is a result of unwanted carbon formation on the inner walls of equipment containing carburizing gas mixtures ( $a_c > 1$ ), and is to a large extent kinetically controlled by the constituents of the alloy surface. Fe, Ni and Co are typical alloying elements that are also good carbon formation catalysts. One strategy for limiting metal dusting corrosion involves creating resistant surface layers or coatings, often stable oxides containing Cr or Al. We have recently worked in this

area in order to establish a more detailed picture on the initial phenomena leading to metal dusting, i.e. establishing the link between the structure and composition of the outmost surface layers and the undesired carbon formation. For Inconel 601 it is found that, depending on the (oxidative) pre-treatment conditions, reducible phases containing Ni and/or Fe may exist inside a predominantly Cr-rich surface layer, and that such a layer may not always be structurally and compositionally stable under conditions relevant to industrial operation [69, 70].

In the case of microchannel reactors metal dusting issues could be enhanced due to increased surface-to-volume ratio and irregularities in the surface structure and composition introduced by the structuring techniques and all the joints created upon sealing structured metallic sheets, rods, blocks or similar by different techniques. Transition zones; i.e inlets, outlets and connections to other process units are also vulnerable. In conventional plants, a compromise between optimum energy recovery and metal dusting are necessary due to this. To our knowledge, results or discussions on the metal dusting issue directly related to microstructured reactors with integrated heat exchange has not been reported in the open literature, but the matter has been under discussion in the scientific community.

We are currently looking into the specific issues related to carbon formation on surfaces relevant to microreactors, Figure 2 displays initial results of carburization experiments performed with pre-treated samples of alloy 800, an alloy type used in microchannel reactor fabrication for high temperature applications [11]. We find that the alloy surface, when covered by a 20-30 nm Cr-rich scale formed during the oxidative pre-treatment, is prone to formation of different forms of carbon on the surface under highly carburizing conditions, yet

somewhat less than a similarly treated Incoloy 601 surface. Moreover, the amount and type of carbon, as well as the interaction with the metallic matrix, varies with the CO exposure temperature. This is illustrated by the SEM images of Figure 2. The Raman spectrum confirm the presence of peaks characteristic to the so-called D, 2D and G peaks of visible excitation, for which the position and ratio is indicative of the type and crystallinity of the carbon [71]. Further results from exposed samples that have been ultrasonically treated to remove all loosely bound carbon (not shown), also demonstrate that part of the carbon is strongly bonded to the surface. Initiation of pitting of the metallic surface has also been observed for the lower exposure temperature. We are proceeding to mapping the link between the initial carbon formations and pitting at more application relevant conditions (presence of H<sub>2</sub> and H<sub>2</sub>O) as well as the catalytic properties of characteristic joints.

### 3. Methanol and DME synthesis

Methanol and DME are important intermediates in the chemical industry for a variety of feedstocks and applications, and they also have potential as fuels in a future of reduced emissions and increased use of renewable energy [72]. Methanol is formed by hydrogenation of CO and/or CO<sub>2</sub>, and the overall reaction is highly exothermic and equilibrium limited under industrial conditions. The dominating catalyst is Cu-based, promoted with Zn(O), and also containing a typical support material such as alumina. This catalyst is remarkably selective given that CH<sub>3</sub>OH is not the thermodynamically favored product, and it also exhibits a cost advantage compared to the other materials active in this reaction: e.g. Pd, Pt. The reaction mechanism and the role of Zn(O) in this system has long been a matter of investigation and debate. Recent prominent theoretical and experimental progress seems, however, to have put several of these issues in place [73, 74]. But due to the relatively low Tamman temperature (680 K) of metallic Cu, the stability of the catalyst remains an issue



[75]. Good control of the temperature is thus imperative to maintain conversion, and moderation of catalyst activity in conventional reactors may be required to avoid hot spots, deactivation, undesirably high outlet temperatures, or even runaway.

Dimethyl ether (DME) can be produced by dehydration of methanol over an acidic catalyst. However, the combination of methanol synthesis and methanol dehydration in a single reactor introduces a process intensification potential by alleviation of the equilibrium limitation in the methanol synthesis. In addition, the number of process units is reduced and the price of feedstock is disconnected from the methanol market, and this has hence been pursued by several researchers and developers [76]. The direct synthesis of DME is overall somewhat more exothermic than methanol synthesis alone, so again the thermal control is essential. A dual function catalyst system is required and approaches range from just physically mixing the two different catalysts to synthesizing the two functions, hydrogenation and dehydration, within the same solid matrix. A compromise of process conditions (C, P, T) that sufficiently facilitate both functions must also be found.

In a long-standing collaboration with Karlsruhe Institute of Technology, integrated micro packed-bed reactor-heat exchangers with different designs were developed and studied in our group for methanol [33-35, 39] and direct DME [36-38, 43-45] synthesis. The reactors were made at KIT by stacking and diffusion bonding etched stainless steel foils to create 1 or 8 reaction slits (typically 6 mm long, 8.8 mm wide and 0.8 or 1.5 mm high) sandwiched between  $0.25 \times 0.5 \text{ mm}^2$  cross section channels for cross flow heat exchange by oil circulation. The reaction slits in some reactors were equipped with hexagonally arranged pillars, and the total reactor void volume was around  $2 \text{ cm}^3$  for the 8-slit modules. The

fabrication and geometry are illustrated in Figure 3. The reactor modules were carefully insulated to minimize heat losses and a high temperature oil thermostat was used to maintain the reactor temperature. Inlet and outlet temperatures were measured and in addition, the different reactors allowed for different approaches to temperature measurement and assessment of thermal gradients: One was a thermocouple well inside the middle reaction slit; another was applying three thermocouple insertion points into the reactor body in close proximity to the reaction zone. A differential pressure transmitter was applied for specific pressure drop measurements [35, 37].

Packed catalyst beds were applied for the high aspect ratio reaction slits. Two porous metallic plates (frits) were installed at the microchannel inlet and outlet to keep the catalyst particles in place and to improve the flow distribution. The catalysts used for methanol or direct DME synthesis were home-made or commercial CuO-ZnO/support, pelletized, crushed and sieved to the desired particle size range (mostly 50–120  $\mu\text{m}$ ) [33-37, 44, 45].  $\gamma$ -alumina [36, 37] or HZSM-5 [44, 45] particles in the same size range were used as methanol dehydration catalyst. A glass model of the slit structure, filled with two differently colored particles with similar particle size, visually indicated that an even particle distribution along such slits can be achieved [35].

The reactions were studied under industrially relevant conditions. The various temperature (profile) measurements adopted indicated gradients of maximum 1-2 K, and Figure 4a demonstrates how the reaction slit temperature (inside the bed) follows the inlet oil temperature during direct DME synthesis. The thermal characteristics of a single reaction slit were also addressed through modeling (Fig. 4a, inset), again indicating uniform temperature

except within a short region at the entrance (2–3 mm) due to a somewhat lower feed gas temperature. The pressure drop (measured at 20 °C) was insignificant relative to the total pressure (50 bar) and showed linear dependence with GHSV to confirm the predicted laminar flow for  $Re=0.1-2$  [35, 37]. Increased total pressure combined with different inert gases was applied to manipulate the diffusivity of the reactants during methanol synthesis [33, 37]. This was done to ensure absence of external mass transfer limitations inside the microchannel geometry and under conditions of low Reynolds number and the stagnant film concept being inapplicable. Hence, circumventing difficulties in applying the conventional assessment methodology, the reactors could be established as practically isothermal, isobaric and free from mass transfer limitations. The remarkable heat removal capacity (see Fig. 4a) of the integrated heat exchange channels also allows methanol and direct DME syntheses under relatively harsh conditions, i.e. high conversion and no catalyst dilution, without hot spot formation and excessive catalyst deactivation.

The residence time distribution (RTD) in the microstructured reactors was investigated by simulation. With the assumption of a uniform catalyst packing throughout the reactor and a uniform flow distribution among the parallel micro channels, a narrow RTD was estimated [34, 35, 37]. The assumptions were based on the previously mentioned visual observations of the catalyst packing in a glass model reactor as well as the high reproducibility of the reactor performance data after re-packing with new batches of a same catalyst. Nevertheless, and as emphasized then, further validation would be desirable. We recently thus proceeded with experimental investigations of the microchannel flow distribution by hot wire anemometry (HWA). By combining the HWA results with those of methanol synthesis experiments, negligible influence from variations in channel dimensions and catalyst particle size on the

performance at industrially relevant conditions could be ascertained [43], i.e. the assumptions seem to hold.

In addition to this, an electrically heated stacked foil microreactor was developed to investigate stacks of 14 catalyst-coated, microchannel foils [39]; each 150 mm long, with 50 200-200  $\mu\text{m}^2$  channels. Sealing to perform methanol synthesis under 80 bar was achieved using a specifically developed housing with graphite seals. Pd/CeO<sub>2</sub> and CuO-ZnO-alumina catalyst coatings were prepared on the interchangeable, structured foils and their performance was compared to similarly prepared catalysts in powder/particle form at industrially relevant, but isothermal, methanol synthesis conditions. No negative effect of the coating procedure was found on the activity or stability, indicating efficient use of the coating layer. When compared to the Cu-based catalyst, the Pd/CeO<sub>2</sub> coating displayed significantly higher initial activity (on a metal mass basis; Pd/Cu) and lower steady-state methanol selectivity. This reflects an interesting relationship between the mechanism and the dispersion and surface structure, with the synthesis resulting in highly active, but less selective Pd nanoparticles that sinter to become more selective for methanol formation [39, 77].

The integrated micro-packed bed reactor-heat exchanger could be established as a suitable reactor geometry for direct synthesis of DME from synthesis gas (Fig. 4b), with the shift of equilibrium limitation on the syngas conversion achieved using  $\gamma$ -alumina [36, 37] as well as HZSM-5 [44] combined with a Cu-based catalyst in physical mixtures. But the investigations also demonstrate that matching the two catalyst functions carries some challenge. HZSM-5, holds extremely high activity per mass or volume as compared to the CuZn catalyst, making it difficult to optimize the mixture with respect to catalyst utilization and mass transfer. The

$\gamma$ -alumina is moderately active and hence matches better the activity of the CuZn system. But the alumina is prone to inhibition by H<sub>2</sub>O and seems to require temperatures somewhat higher than acceptable with respect to controlling Cu sintering.

Further exploring the possible effect of the two reactions on each other, it could be shown that the dehydration reaction negatively affected the methanol formation kinetics. Investigating the cause of this eliminated all possibilities but the increase partial pressure of H<sub>2</sub>O due to dehydration, causing similar effects as increased steam or CO<sub>2</sub> content in a methanol synthesis reaction feed [44]. Addressing possible deactivation mechanisms under industrially relevant conditions, particular effects from mixing the two catalysts could not be verified; i.e. effects of the reactant mixture or the catalyst constituents. Sintering remains the main deactivation issue for the Cu-based system given absence of typical poisons in the synthesis gas [45]. Throughout our investigations we have also tried to exclude or confirm the possibility of metal transfer from the reactor walls, which could potentially increase due to the large surface-to-volume ratio. Ni and Fe are elements susceptible to transfer level by volatilization or carbonyl formation from steel or catalysts. Cu catalysts are known as particularly sensitive to such effects, since they would accumulate on the surface and affect the selectivity. We have not been able to confirm this by analysis of used catalyst by XPS or other techniques within the achievable time-on-stream and sensitivity levels.

The high activity of HZSM-5 makes it difficult to study the combined methanol synthesis and methanol dehydration with the methanol dehydration rate controlling the overall reaction. Experiments in the microchannel reactor with dehydration of methanol to DME only were therefore designed to simulate the direct synthesis under DME formation control [45]. The

results indicated accumulation of hydrocarbon species formed on strong acid sites and confined within the pore system as the main deactivation issue with HZSM-5, but effects of the syngas composition ( $H_2/CO$ ) on this phenomenon could not be ruled out. Given that the formation of such hydrocarbon side products is influenced by the residence time distribution, dehydration in microchannels may even be considered interesting for a two-step process, but such investigation could not be found in the literature. Finally, modification by ion exchange (Na) can be performed to moderate the activity of the zeolite in direct synthesis experiments, and was also found to suppress deactivation [45].

Effects of the catalyst constituents on each other have been reported by others, but then in the case of enhanced contact between the phases through synthesis or mechanical processing (grinding, pelletizing, slurring, etc.) [78]. Moreover, recent results presented of Topsøe's direct DME the development process confirmed the migration of Zn into the zeolite structure. Because extensive deactivation studies are elaborate and time-consuming, such deactivation cannot be completely ruled out also in the case of physical mixtures. But it may be less of an issue in a microchannel reactor due to that a well-mixed matrix of methanol synthesis and methanol dehydration catalyst can be applied without mechanical (e.g. pelletizing) or chemical approaches for ensuring the proximity of the two functions while simultaneously maintaining low pressure drop and good mass transfer.

#### **4. Fischer-Tropsch synthesis (FTS)**

The Fischer-Tropsch synthesis converts synthesis gas ( $CO+H_2$ ) to hydrocarbons (and some oxygenates) at a temperature between 200-350 °C in the pressure range 20-30 bar. It provides a way to produce liquid fuels and chemicals from coal, natural gas and biomass feedstock;

value chains that may be referred to as CTL, GTL and BTL, respectively. Known catalysts for FTS are Ni, Fe, Co and Ru, and the reaction follows a stepwise polymerization mechanism resulting in an Andersen-Schulz-Flory (ASF) type product distribution. Commercial catalysts are exclusively Fe or Co based. Fe is suited for CTL and BTL with low  $H_2/CO$  due to its high water-gas shift activity. Co is preferred for GTL with  $H_2/CO \sim 2$  owing to its high activity and  $C_{5+}$  selectivity, good stability and low water-gas-shift activity [79]. The FTS reaction is strongly exothermic and the product distribution is sensitive to temperature and pressure. In order to maximize the desired products and maintain catalyst stability, heat exchange and temperature thus need to be precisely controlled.

FTS has been commercialized in South Africa (Sasol Sasolburg/Secunda CTL)[80], Malaysia (Shell Bintulu GTL)[81] and Qatar (Sasol Oryx GTL, Shell Pearl GTL)[82] for fuel production in the scale of between 12,000-140,000 barrels per day. Oryx is based on a slurry phase reactor type whereas Pearl uses multi-tubular fixed-bed reactors; both concepts with advantages and disadvantages. While the main challenge with the former is the separation of fine catalyst particles from the liquid product, the latter may suffer from insufficient heat removal. These technologies, along with the rest of the process train, are targeted for large gas fields. It has been estimated that less than 10% of the world's gas fields are large enough to sustain a 10,000 bpd GTL facility [83].

In order to utilize a wider range of on-shore and off-shore gas resources, as well as biomass, small-scale and modular systems suited for 500-2000/10000 barrels per day capacity are of great interest. Microchannel reactors can provide scalable and safe heat integrated, compact systems that can reach high productivity per volume of reactor. The superior heat transfer

allows prevention of hot-spot and run-away issues, which are detrimental to the selectivity to desired products and the catalyst stability in FTS. Main research efforts in the microchannel technology concern proof-of-concept studies, catalyst development and regeneration, scale up and commercialization.

Using the integrated micro packed-bed reactor-heat exchangers with 800  $\mu\text{m}$  channel height described above and applied for methanol and direct DME synthesis, Myrstad et al. investigated highly active 53-90  $\mu\text{m}$  Co-Re/ $\text{Al}_2\text{O}_3$  catalyst particles containing 20 or 40 wt% cobalt and 0.5 or 1 wt% Re, respectively, for FTS [84]. Stable, high conversion and  $\text{C}_{5+}$  selectivity were maintained over more than 40 h. Compared to a fixed bed, equivalent conversion and selectivity was achieved at 20 K lower reaction temperature, owing to the improved thermal management of the reactor, and hence avoiding local overheating of the catalyst. In addition, a pressure drop of less than 1.25bar/m was observed, even under the highest GHSV applied (20000 N ml/g/h) and catalysts particle size of 53-75 $\mu\text{m}$ . There is, however, a balance between heat and mass transfer and pressure drop with respect to the channel size. J. Knochen et al. [85] investigated FTS over 19wt%Co-1wt%Re/ $\text{Al}_2\text{O}_3$  catalysts in a millistructured fixed bed reactor with separate heat exchange channel. Their numerical simulation indicated that efficient heat removal is still possible in channels of 3 mm width, while catalyst particles of 350  $\mu\text{m}$  size allow high effectiveness factors at acceptable pressure drop by numerical simulation. Chambrey et al. compared a milli-fixed bed with a conventional centimetric fixed bed (channel dimension in mm or cm range, respectively) and a slurry bubble column reactor using the same Co-Pt/ $\text{Al}_2\text{O}_3$  catalyst at 493 K and 20 bar and  $\text{H}_2/\text{CO} = 2$  [86]. The higher initial Fischer–Tropsch reaction rate displayed in the single channel milli-fixed bed reactor was attributed to better temperature control. The milli-fixed bed reactor had similar apparent deactivation behavior as the slurry stirred tank, while the



centimetric fixed bed experienced considerable deactivation due to uncontrolled temperature peaking during start up.

The microchannel productivity, selectivity and catalysts stability nevertheless depends on the reaction conditions. Recently, a 40%Co1%Re catalyst supported on  $\gamma$ -alumina was tested in our microchannel heat exchange reactor at 210 °C; 20, 30 and 40 bar pressure, and GHSV of 7557-22624 N ml/g/h [87]. The increase in pressure from 20 bar reduced the C<sub>5+</sub> selectivity, while the methane selectivity remained more or less constant. Instead, enhanced formation of C<sub>2</sub>-C<sub>4</sub> hydrocarbons, especially C<sub>2</sub>-C<sub>4</sub> olefins, was observed as shown in Figure 5a The C<sub>2</sub>-C<sub>4</sub> paraffin formation was also slightly enhanced at higher pressure. The catalyst proved itself relatively stable at all the tested conditions, and this is indicated from Figure 5b. The work demonstrates that in order to achieve optimum productivity and stability, the process conditions in a microchannel reactor can be optimized based on the chosen catalyst.

In order to fully utilize the benefits of microchannel technology, also the catalyst has to be properly optimized. Conventional commercial catalysts for slurry or fixed-bed reactors contain 15-40 wt% Co, usually promoted with 0.5-1 wt% noble metal to improve reducibility, and in certain cases the selectivity of the catalyst [88-90]. The productivity in the commercial multi-tubular fixed-bed reactor is typically limited by the heat removal capacity. For experiments, the catalyst is normally mixed with significant amounts of inert material (SiC, or similar) to ensure isothermal conditions. For microchannel reactors, it is possible to use a highly active system, for instance 40wt%Co without any dilution with SiC. The FTS performance of a 40%Co1%Re catalyst supported on  $\gamma$ -alumina in a microstructured packed bed reactor was compared with that in an electrically heated laboratory scale, highly diluted

fixed-bed reactor under similar conditions [91]. Similar activity and C<sub>5+</sub> selectivity were achieved in the microchannel reaction without any dilution. The reactor productivity not only depends on the active metal loading, but also on the exposed active surface, i.e, the metal dispersion. Catalyst synthesis by conventional incipient wetness impregnation often leads to lower dispersion upon pushing the metal loading. Velocys therefore proceeded to develop a novel organic matrix combustion method to prepare cobalt based catalysts with high loading (>40wt%Co) while maintaining optimum cobalt particle size/dispersion [92]. The relatively small Co particle size (~ 6nm) and narrow particle size distribution ensure high activity and good stability, as displayed in Figure 6b [93]. An illustration of Velocys microchannel cross flow reactor for FTS is shown in Figure 6a [94].

Catalyst deactivation and regeneration in the microchannel reactor is an important issue commercially, and the cobalt based catalysts typically go through an initial rapid deactivation followed by a slow long-term deactivation. Tsakoumis et al. [95] reviewed the deactivation mechanisms of cobalt based catalysts in FTS as summarized to poisoning, re-oxidation of cobalt active sites, formation of surface carbon species, carburization, surface reconstruction and sintering of cobalt, metal–support solid state reactions, and attrition. Sulfur poisoning is well-known, and usually lead to permanent deactivation of the FT catalysts. Therefore the limit for sulfur containing compounds in syngas is usually restricted to 0.02 mg/m<sup>3</sup> [96]. Sulfur poisoning could be a more severe issue when using microchannel reactor since it is more difficult to load and unload the catalysts. Hence, it is important to remove sulfur upstream especially when using biomass based syngas. The extent of sintering, re-oxidation, cobalt–support mixed compound formation and carbon formation typically depend on the type of support and reactions conditions. With respect to deactivation of cobalt catalysts for low temperature (LT) FTS, two main long-term deactivation mechanisms were recently

examined with respect to their commercial relevance; carbon deposits covering the catalytic surface and re-oxidation of metallic cobalt [97]. It was concluded that polycarbon deposition is the principal long-term cause of deactivation for all commercial catalysts and reactor types, since the catalysts are typically designed to be stabilized against oxidation at industrial conditions, i.e. relatively high conversion (~70%). Reduction upon exposure to syngas, as well as sintering, were categorized as short-term phenomena determining the steady-state activity after 1–2 months of TOS. Although deactivation during the first 6–18 months of operation can cause 30–60% loss in activity in cobalt-based LT FTS catalysts, it appears possible to regenerate the catalyst to approach the activity of a freshly conditioned catalyst for slurry phase, fixed bed as well as the emerging microchannel reactors. Velocys demonstrated that *in-situ* regeneration of highly active cobalt based catalysts is effective after 650 days on stream in a laboratory microchannel unit [98]. As shown in Figure 6c, partial recovery of activity was noted with regeneration in hydrogen while an oxidative treatment completely recovered the catalyst activity. From the regeneration method, it is likely that both carbon formation and sintering has played a role in the catalyst deactivation in the microchannel reactor.

For intensification of the mass transfer in multiphase reactors, alternative catalyst geometries like honeycombs, monoliths, structured packings or foams etc. have also been proposed [86]. Monolithic reactors made of different materials, microchannel reactors and hierarchically structured carbon nanofibers/carbon felt (CNF/CF) composite as a reactor were compared in FTS over cobalt based catalysts promoted with Re. The support material was  $\gamma$ -alumina for monolith and microchannel reactor and cobalt on silica coated carbon nanofiber-graphite felt composite for the CNF/CF reactor [41, 42, 84]. All reactor types showed activity and selectivity consistent with results from standard (diluted) fixed-bed reactor experiments, and

efficient heat removal and elimination of diffusional limitations could be obtained without measures such as dilution by inert material [41]. L.C. Almeida et al. [99] also studied the effect of different supports (aluminum foams of 40 ppi (pores per square inches), honeycomb monolith, micromonolith of 350 and 1180 cpsi (cells per square inches) and microchannel block, respectively) loaded with washcoats of a 20%Co–0.5%Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst on FTS. The methane selectivity increased with the thickness of the washcoat for all reactor types due to the higher effective H<sub>2</sub>/CO ratio over the active sites resulting from the higher diffusivity of H<sub>2</sub> compared with CO in the liquid products filling the pores.

Combined with highly active and stable catalysts, microchannel reactors with efficient mass and heat transfer can achieve high volume-based productivity and therefore process intensification. In addition, the scale up of microchannel reactor by adding more operation units is more straightforward. The scale up of microchannel reactors for FTS has been demonstrated using reactors of different length and number of channels by Velocys [100]. Similar CO conversion, product selectivity and chain growth probability has been observed at different scales ranging from ~0.004 to ~1.5 gallons per day. Extensive tests at laboratory and pilot plant scale, including during upset, transient and large variety of process conditions have shown that high selectivity could be maintained at high productivity. Both Velocys and CompactGTL are among the key players in building small-scale GTL plants [7]. Velocys commercial reference plant utilizing landfill gas and natural gas as feedstock is under construction in Oklahoma, Ohio; while Compact GTL has been projecting a GTL plant in Kazakhstan using natural gas that would otherwise be flared.

## 5. Conclusions

Research into the characteristics and potentials of microstructured reactor with enhanced mass and heat transfer properties in the production of synthesis gas and its conversion into value-added products has been summarized. Our and other's efforts in this area show that while conversion of synthesis gas to methanol, DME or Fischer-Tropsch products in microchannels is promising technology for enabling small-scale GTL and BTL operation, synthesis gas production technology remains a challenge. The results presented point to the reasons behind this.

For syngas generation, promising results in terms of temperature profile, product selectivity, carbon formation and stability during cycling have been obtained applying microchannel monoliths in partial oxidation and oxidative steam reforming of lower hydrocarbons. Choice of high temperature alloy and method of alumina coating preparation was essential to this. The results also point to potential for suppressing gas phase reactions at high temperature. Metal dusting corrosion is proposed as an important issue that may in particular impact microchannel reactors for methane steam reforming with intensified performance by superior heat exchange geometries. This is partly due to the increased surface area, but also related to combinations of surface structure and composition with the (local) reaction environment (C;P;T) that may arise inside or connecting to the catalytic reaction volume. This is shown by work concerning carbon formation on alloy 800, which appears as a reasonable choice of material.

With respect to the exothermic syntheses of methanol, DME or Fischer-Tropsch products, a microchannel design with integrated, cross-flow heat exchange can be established as a

practically isothermal, isobaric reaction environment free from internal or external mass transfer limitations. The different catalysts may therefore be utilized to achieve high volumetric and gravimetric productivity without introducing accelerated deactivation. We have not been able to verify additional deactivation issues from the materials or the reaction environment and numerical and experimental investigations into the flow distribution are also encouraging.

Alleviation of the methanol synthesis equilibrium limitation by mixing a CuO-ZnO/supportcatalyst with dehydration catalysts ( $\gamma$ -alumina or HZSM-5) has been demonstrated. The microreactor has also shown its usefulness as a research tool when being able to establish – with the methanol reaction as the limiting – how the H<sub>2</sub>O formation from dehydration affects the kinetics of methanol formation. The same was the case when addressing which deactivation mechanisms that may be relevant for a hybrid physical mixture direct DME catalyst in a micro packed-bed reaction environment.

Finally, with respect to Fischer-Tropsch synthesis, microchannel reactors enable usage of highly active catalysts and allow process conversion up to 90% without thermal runaway or significant deactivation of the catalysts. Our results also show that pressure impacts the C<sub>5+</sub> selectivity over 40%Co1%Re- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under specific conditions in a microchannel reactor. The scale up of the microchannel technology for FTS has been shown promising by changing the length of or adding up channels, and lab and pilot scale testing facilitate first commercial reference plant to be constructed in Oklahoma. In addition, it the possibility of in-situ regeneration of cobalt based catalyst after long-term process has been demonstrated by Velocys..

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## Figure captions

**Figure 1:** Microchannel Rh/Al<sub>2</sub>O<sub>3</sub>/Fecralloy monolith for catalytic partial oxidation (POX) and oxidative steam reforming (OSR) of hydrocarbons. a) Reactor geometry and appearance inside during experiments at high temperature. b-d) Results obtained during POX of propane; b) Temperature profiles for different furnace temperatures with vertical lines representing the extent of the monolith; c) Reactant conversion and selectivity to main products; d) By-product selectivity. e) SEM micrograph of an individual microchannel from a monolith used in repeated experiments,

**Figure 2:** SEM images (a, c, d) and Raman spectrum (b) of the surface of Alloy 800 after first polishing, then oxidation (10% H<sub>2</sub>O in Ar, 540 °C, 1 bar for 6 h), and finally exposure to a highly carburizing gas mixture (100Nml/min 10% CO in Ar, 1 bar for 20 h) at (a, b) 550 °C; (c, d) 650 °C

**Figure 3:** Illustration of the stainless steel microchannel reactor with integrated heat exchange channels for oil circulation. a) Principal geometry of the reaction and heat exchange channels; b) Stacking, bonding sealing and assembly; c) Reactor top view; inlet of reaction slits without catalyst; d) Complete reactor with connections

**Figure 4:** Direct synthesis of DME over a mixture of methanol synthesis and methanol dehydration catalyst in a microchannel reactor with integrated heat exchange. a) Correlation between set inlet temperature and measured reaction slit temperature, point of measurement illustrated in picture. Insert show temperature profile simulation, with a gradient of less than 2K (50-80 μm CuO-ZnO-support + γ-Al<sub>2</sub>O<sub>3</sub>). b) CO conversion (measure and equilibrium) as a function of temperature for methanol and direct DME synthesis (80-125μm CuO-ZnO-support + HZSM-5) at 50 bar total pressure, feed H<sub>2</sub>:CO:CO<sub>2</sub>:CH<sub>4</sub>:N<sub>2</sub>=56:28:5:6:5 (mol.%), and identical SV based on the Cu cat. mass.

**Figure 5:** a) Effect of pressure on the selectivity to C<sub>5+</sub> and CH<sub>4</sub> over a 40%Co-1%Re/γ-Al<sub>2</sub>O<sub>3</sub> catalyst at 210 °C, b) CO conversion and C<sub>5+</sub> selectivity as a function of time on stream at a variety of reaction conditions (temperature of 210 °C and 225 °C and total pressure of 20, 30 and 40 bar).

**Figure 6:** a) Illustration of a Velocys microchannel cross flow reactor for FTS[1], b) Co<sub>3</sub>O<sub>4</sub> particle size distribution as prepared by organic matrix combustion and conventional incipient wetness impregnation[2], c) CO conversion and CH<sub>4</sub> selectivity over 2 years of operation in a laboratory microchannel unit with regeneration at about 650 days on stream. Courtesy of Velocys, Inc.

Figure 1

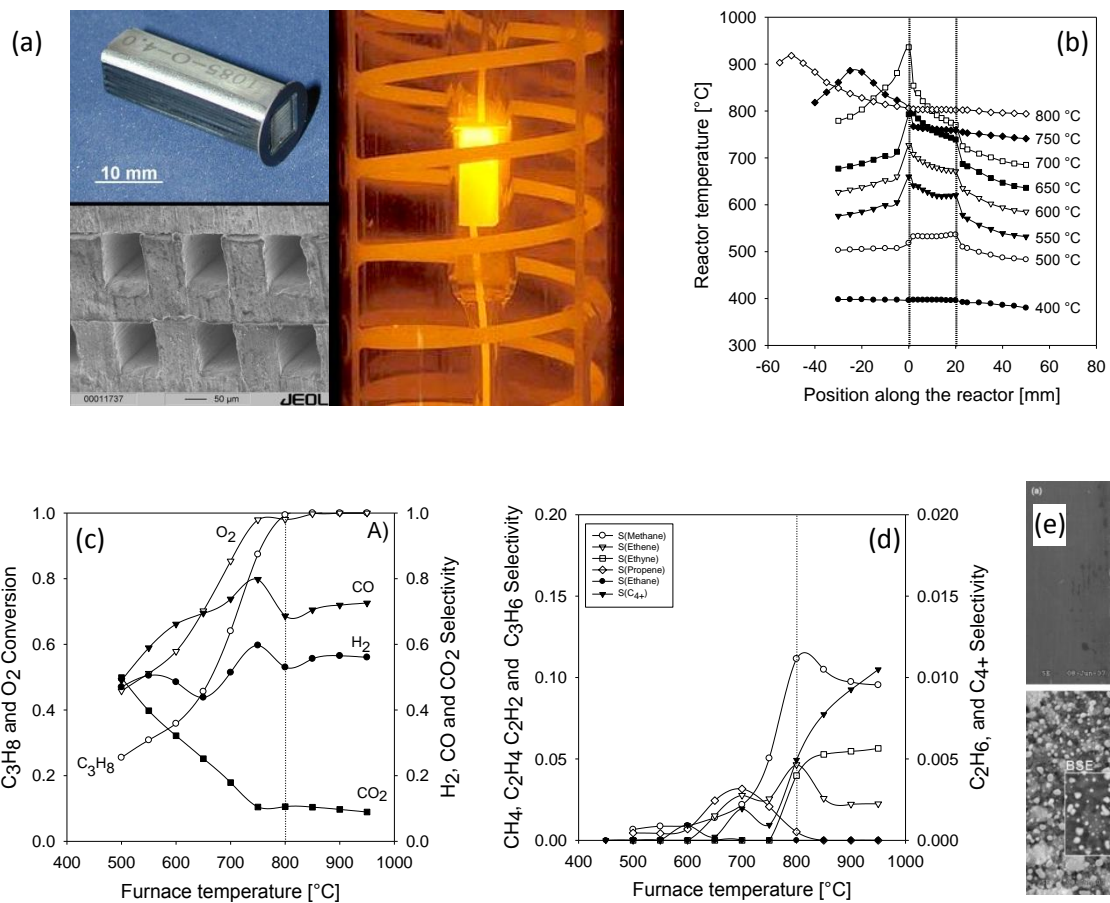




Figure 2

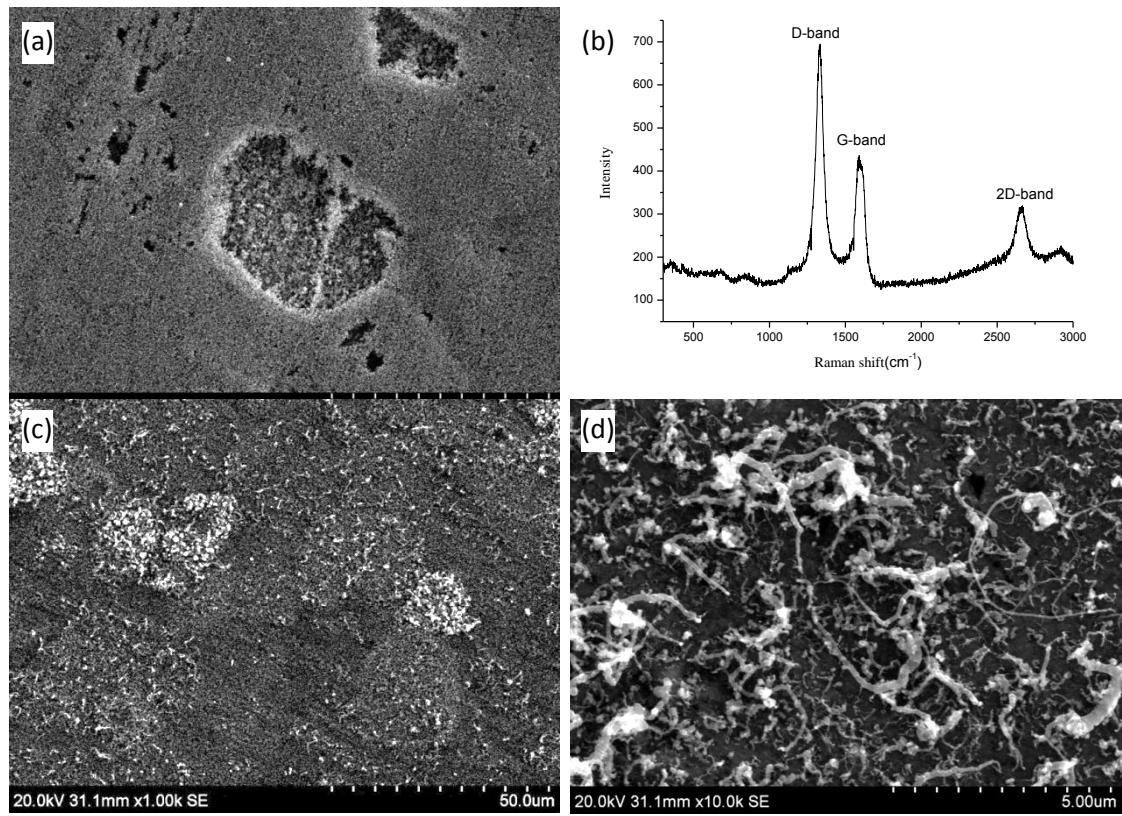


Figure 3

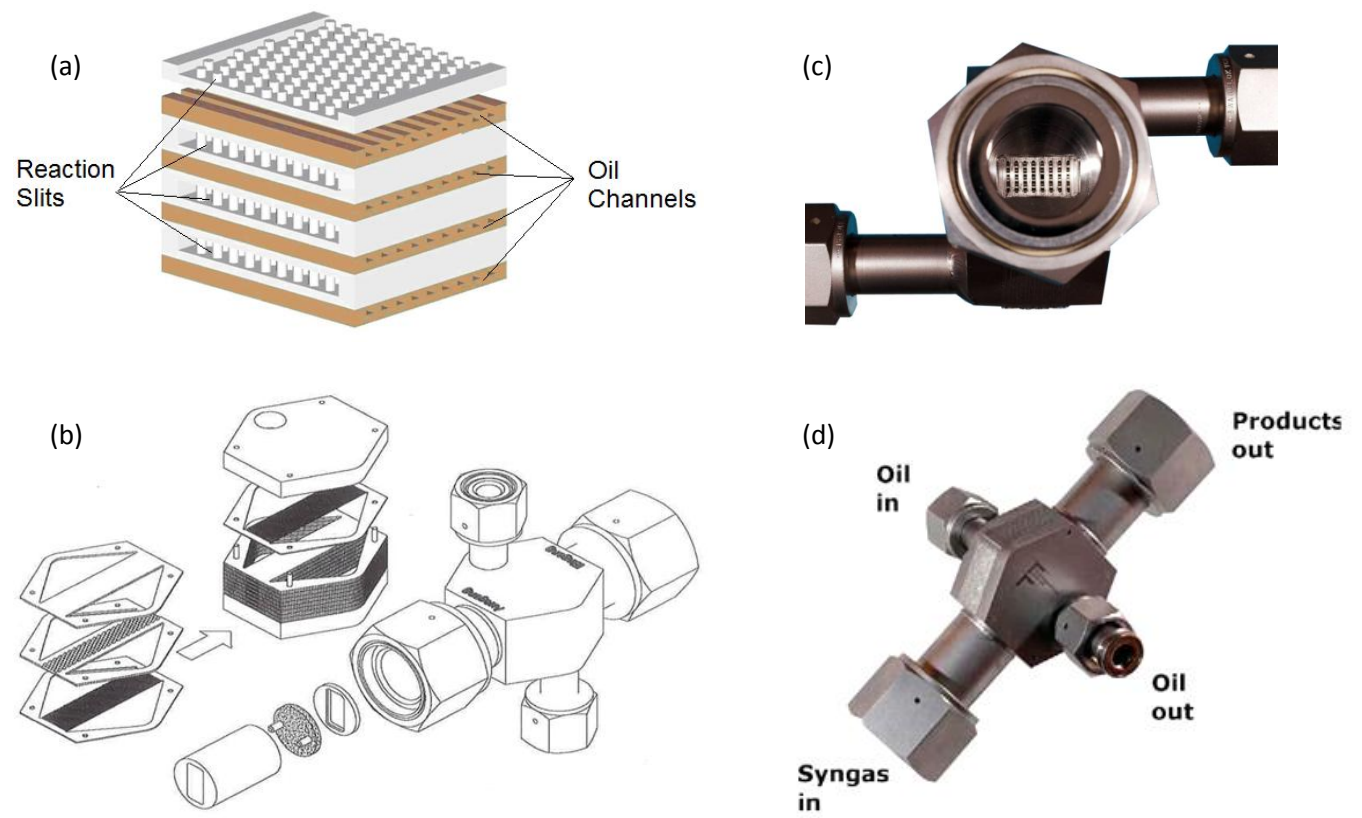


Figure 4

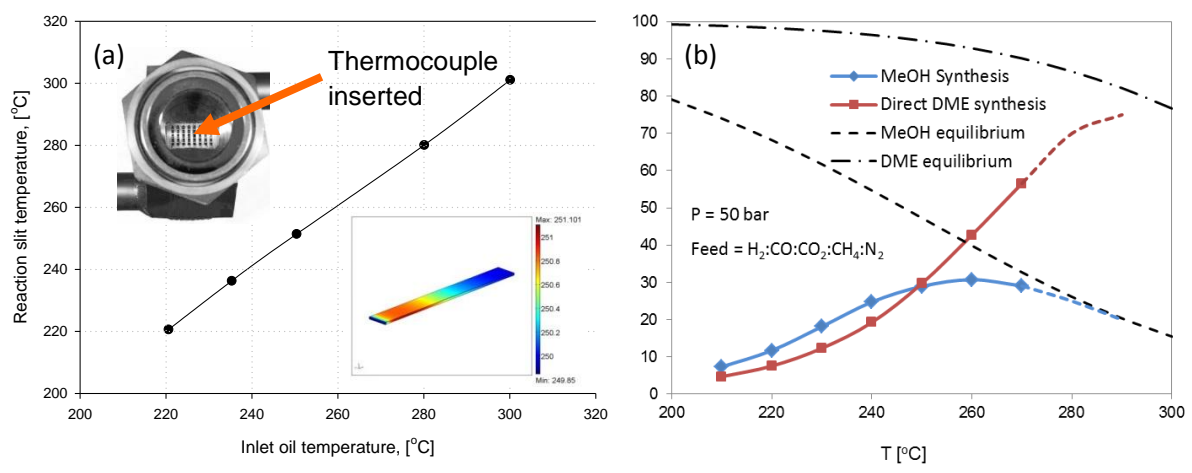


Figure 5

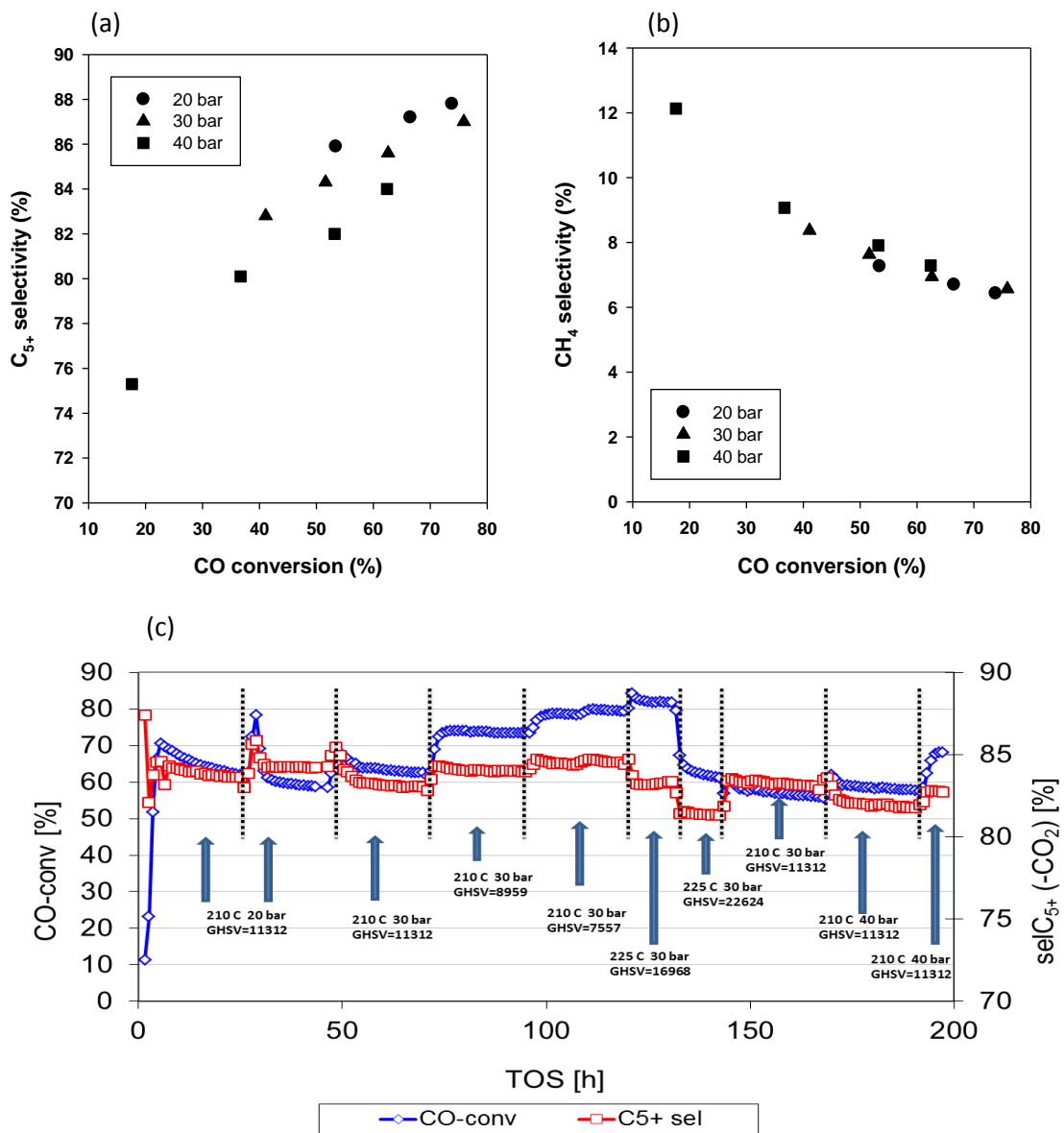
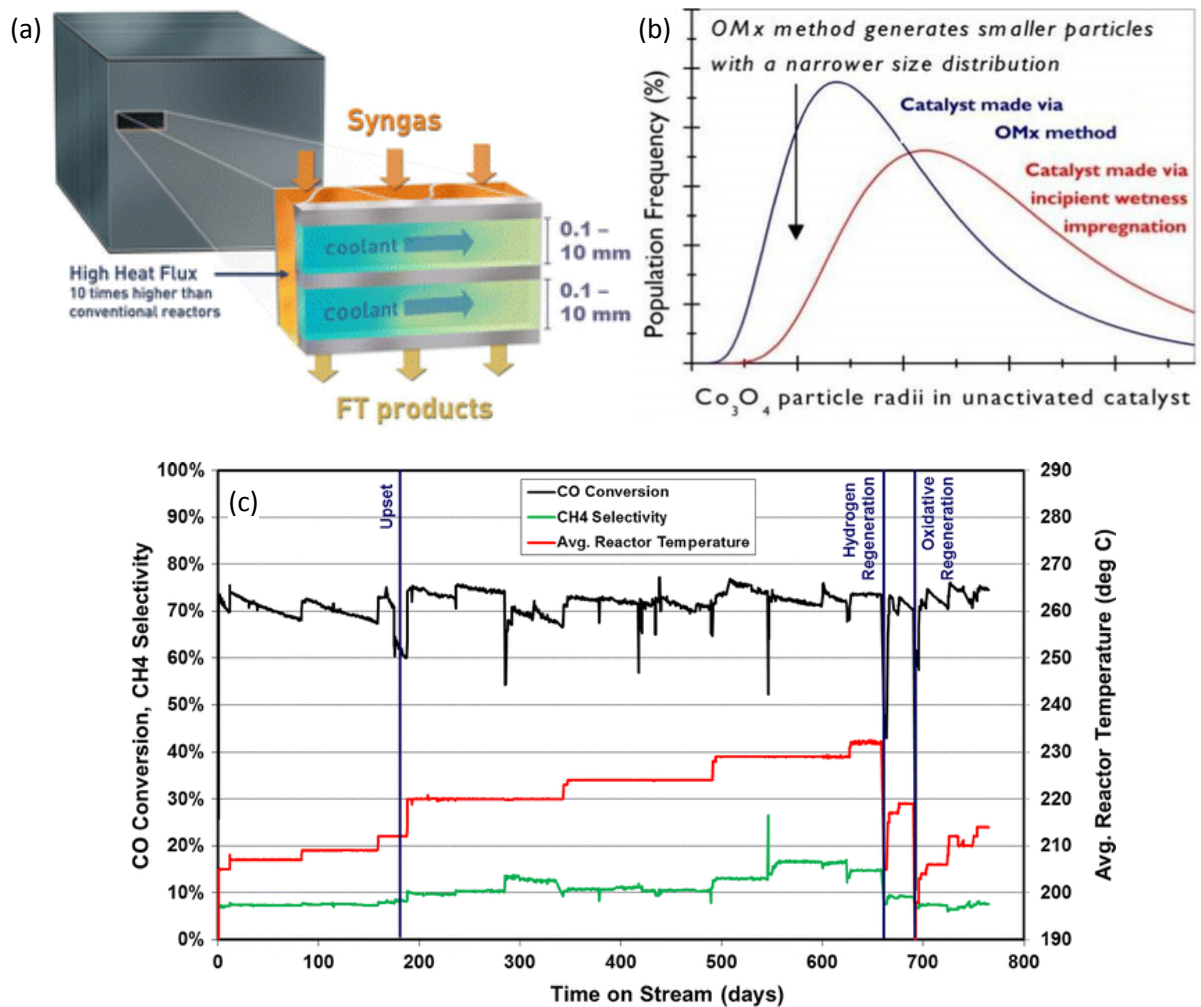


Figure 6



1. LeViness, S., et al., *Velocys Fischer-Tropsch Synthesis Technology—New Advances on State-of-the-Art*. Topics in Catalysis, 2014. **57**(6): p. 518-525.
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