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# Fischer–Tropsch synthesis in milli-fixed bed reactor: Comparison with centimetric fixed bed and slurry stirred tank reactors

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ABSTRACT

This paper presents a comparative study of Fischer–Tropsch synthesis in single channel milli-fixed bed, conventional centimetric fixed bed and slurry stirred tank reactors. In the three reactors, the catalytic measurements were carried out with the same conventional platinum-promoted alumina supported cobalt catalyst at 493 K and 20 bar using a stoichiometric syngas ratio ($H_2/CO = 2$). The single channel milli-fixed bed reactor displays a higher initial Fischer–Tropsch reaction rate than the conventional centimetric fixed bed reactor. This effect was assigned to a better temperature control and less significant catalyst deactivation during the startup of the single channel milli-fixed bed reactor. The slurry stirred tank reactor shows much lower hydrocarbon productivity than the milli- and centimetric fixed bed reactors, which is probably due to incomplete catalyst reduction. A considerable catalyst deactivation due to the uncontrolled temperature hike can occur during the reactor startup in the conventional centimetric fixed bed reactor. The slurry stirred tank and milli-fixed bed reactors show similar apparent deactivation behavior.



## 1. Introduction

Indirect conversion of natural syngas into hydrocarbons via Gas-to-Liquids (GTL) technology and Fischer–Tropsch synthesis (FT) is currently one of the most promising and environmentally effective solutions to the problem of finding suitable substitutes for liquid clean fuels. Multi-tubular fixed bed and slurry bubble column reactors have been currently used on industrial scale in South Africa, Malaysia and Qatar for this highly exothermic reaction [1–8]. Both fixed bed and slurry reactor technologies present several serious drawbacks. Wax-catalyst separation, highly demanding scaling-up, catalyst deactivation and attrition are the major barriers inherent to the use of slurry bubble column reactor. The fixed-bed multi-tubular reactor suffers from higher cost, insufficient heat removal, diffusion limitations and pressure drop. A conventional fixed bed reactor with internal tube diameter of several centimeters filled with catalyst pellets exhibits significant axial and radial temperature gradients which may lead to higher production of methane, lower selectivity to long chain hydrocarbons and a shorter catalyst life.

Due to several disadvantages of both reactor systems, new concepts are presently investigated. For intensification of mass transfer properties of multiphase reactors, alternative catalyst geometries like honeycombs, monoliths, structured packings or foams have been proposed [9–13]. In the micro-structured reactor the catalyst can be loaded by coating the reactor walls or by placing small catalyst powder in the micro-fixed bed. It has been shown that coated micro-reactors allow reducing the pressure drop and improving the heat transfer. Holmen et al. [14] previously found that the reactors wash-coated with FT catalysts could have catalytic performance similar to that observed with powdered catalysts. The reactors with layer thicker than about 50 μm suffer however, from diffusion limitations, accompanied by the expected decrease in the apparent activation energy [9,14,15]. The conventional proven FT catalysts cannot be used directly in coated micro-reactors. The mechanical and chemical resistance of catalyst coatings at a wide range of temperatures and in the presence of reagents and reaction products could be a challenge because of the difference in thermal expansion coefficients and catalyst stability. In addition, the catalyst inventory, i.e. ratio of catalyst to reactor volume, in the coated micro-reactor is often insufficient to attain satisfactory hydrocarbon productivity. Thus, to become commercially attractive, the ratio of catalyst and reactor volume in coated micro-reactors and hydrocarbon productivity should be significantly increased [16].

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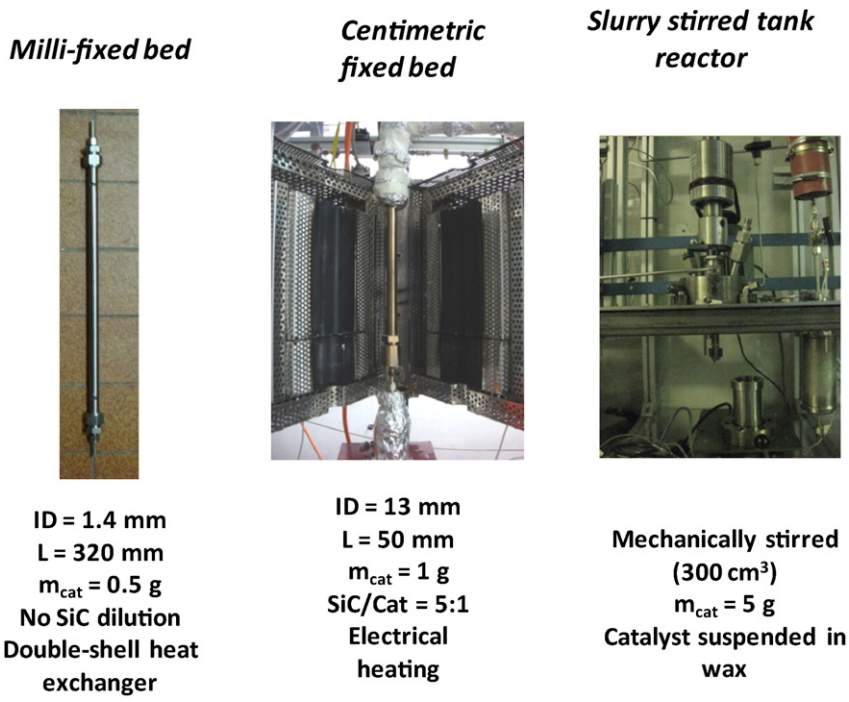


**Fig. 1.** Principal characteristics of laboratory reactors for FT synthesis.

The micro-fixed bed reactor has a number of advantages relative to the coated micro-reactors, such as higher catalyst inventory, use of proven efficient Fischer–Tropsch catalysts, easier reactor loading and possible catalyst replacement [17]. Note that the coated micro-reactors require specifically designed catalysts. The catalyst deposition on reactor wall can be challenging. On the other hand, micro-fixed bed reactors can show a significant pressure drop especially at higher flow rates and less efficient heat removal than coated micro-reactors. The capability of micro-structured packed bed reactor to operate with a highly active cobalt catalyst under severe conditions has been recently demonstrated by Myrsrad et al. [18]. Encouraging results with micro- and milli-structured fixed bed reactors on the scale of both laboratory and pilot FT units have been repeatedly reported by Velocys, Inc. [19].

Although the enhancement of heat transfer has been usually reported for the reactors with inner diameter smaller than 1 mm, several examples suggest that a sufficient degree of process intensification can be obtained with reactors of characteristic length of a few millimeters. The advantages of a milli-fixed bed reactor relative to micro-fixed bed counterparts are related to a lower pressure drop because of using larger catalyst pellets, simpler design and easier catalyst loading/discharging. Knochen et al. [20] showed that efficient heat removal in FT synthesis is possible even with reactor channel width of 3 mm and the pressure drop can be acceptable with particle sizes of 100 μm. The present work focuses on the particularities of FT synthesis in a single channel milli-fixed bed reactor. An attempt has been made to get new insights into the possible advantages of milli-fixed bed reactors relative to more conventional centimetric fixed bed and slurry stirred tank reactors.

## 2. Experimental

Carbon monoxide hydrogenation was carried out in three different stainless steel reactors (Fig. 1): a tubular milli-fixed bed reactor (ID = 1.4 mm, $L$ = 320 mm), a centimetric tubular fixed bed reactor (ID = 13 mm, $L$ = 400 mm) and a slurry stirred tank reactor (300 $cm^3$, radial impeller) [21] under identical operating conditions. The same laboratory-made Co(25%)Pt(0.1%)/$Al_2O_3$ catalyst was used in milli-fixed bed, centimetric fixed bed and slurry phase reactors. The catalyst was synthesized via incipient wetness co-impregnation; its preparation and characterization details are available elsewhere [22]. To minimize formation of heat spots the catalyst was diluted with SiC (5:1) in the centimetric fixed bed reactor, whereas non diluted catalyst was used in the milli-fixed bed and slurry stirred tank reactors. The validity of chemical regime was checked in all the reactors.

The isothermal regime in milli-fixed bed and centimetric fixed bed reactors was verified using the Mears criterion for neglecting radial temperature gradient [23,24]. When this criterion is fulfilled, the radial temperature profile is assumed to be flat, while the presence of heat spots along the bed cannot be excluded:

$$(1-\varepsilon) r_P \left|\Delta H_R\right| \frac{T_A d_t^2}{4\lambda_{er}^{sf} T_p^2} \left(1 + \frac{8\lambda_{er}^{sf}}{U d_t}\right) < 0,4$$

Calculation for centimetric fixed bed reactor with (5:1) catalyst dilution with SiC gives the Mears criteria of 2.0 assuming 60% carbon monoxide conversion, 60 N $cm^3$/min carbon monoxide flow rate and using the following parameters [23]: rate of reaction $r_p$ = 3.4 mol $s^{-1}$ $m^{-3}{}_{cat}$ (with catalyst dilution), void fraction of the catalyst $\varepsilon$ = 0.4, reaction enthalpy $\Delta H_R$ = −165 kJ $mol^{-1}$, adiabatic temperature $T_a$ = 14,400 K, tube diameter $d_t$ = 0.0125 m, global heat exchange coefficient $U$ = 400 W $m^{-2}$ $K^{-1}$, effective radial thermal conductivity $\lambda^{sf}{}_{er}$ = 1 W $m^{-1}$ $K^{-1}$ and reactor wall temperature $T_p$ = 493 K. The analogous estimation for the single channel milli-fixed bed reactor ($d_t$ = 0.0014 m, same thermal parameters) yields the Mears criteria of 1.43 (with $r_p$ = 17.7 mol $s^{-1}$ $m^{-3}{}_{cat}$). Calculations suggest the presence of radial temperature gradient of about 0.5 K in both reactors.

The FT operating temperature and pressure in all the three reactors were respectively 493 K and 20 bar. The catalyst loading was 0.5 g and 1.0 g in the milli- and centimetric fixed reactors and 5.0 g in the slurry stirred tank reactor. Before the reaction the catalyst