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Intensifying heat transfer in Fischer-Tropsch tubular reactors through the adoption of conductive packed foams

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HIGHLIGHTS

- Highly conductive open-cell foams enhance heat transfer in packed-bed FTS reactors.
- Packed-foams enable running the FTS under severe conditions with excellent T-control.
- Thermal runaway occurs under mild conditions in conventional packed-bed reactor.
- Packed-foams provide an innovative solution to increase the catalyst inventory.
- Conductive packed foams are an efficient strategy for compact tubular reactor units.

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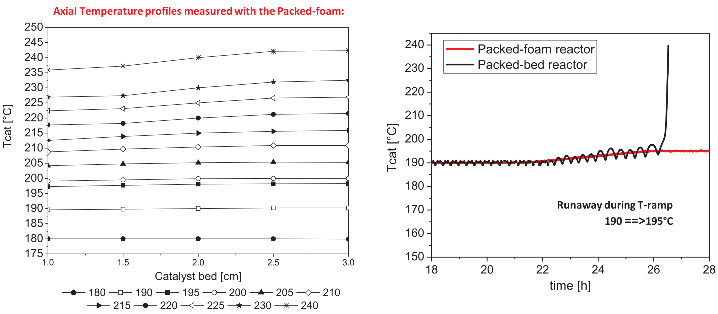
GRAPHICAL ABSTRACT



ABSTRACT

The low-temperature Fischer-Tropsch synthesis is a strongly exothermic process wherein the temperature control is a crucial issue. In this work, we demonstrate experimentally for the first time the adoption of a Fischer-Tropsch tubular reactor (2.78 cm I.D.) loaded with a highly conductive open-cell aluminum foam packed with catalyst microspheres to enhance heat exchange. Accordingly, the performances of a highly active Co/Pt/Al_2O_3 catalyst packed into the metallic structure are assessed at industrially relevant operating conditions and compared with those obtained in a conventional randomly packed fixed-bed reactor. The structured catalyst reaches outstanding performances (duties in excess of 1300 kW/m^3 with CO conversions > 65%) with a remarkable temperature control. Almost flat axial temperature profiles are measured along the catalytic bed even under the most severe process conditions, showing the excellent ability of the "highly conductive packed-foam reactor" concept to manage the strong exothermicity of the reaction. In contrast, when the same experiment is carried out over the same Co/Pt/Al_2O_3 catalyst just randomly packed in the reactor, an abrupt increase of the catalyst temperature occurs already at low temperature, eventually leading to thermal runaway. The results herein collected prove the potential of conductive metal foams as enhanced reactor internals for the intensification of strongly exothermic processes in nonadiabatic tubular reactors. Furthermore, the "packed-foam" configuration also demonstrates the possibility to overcome the inherently limited catalyst inventory of the washcoated conductive structured reactors proposed so far, thus boosting the productivity per reactor volume.

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1. Introduction

The low-temperature Fischer-Tropsch synthesis (FTS) is the well-known catalytic reaction which involves the hydrogenation of carbon monoxide over cobalt metal centers with the formation of long-chain hydrocarbons and water [1]. In the last decade, the interest in the FTS has been considerably renewed in view of exploiting both associated and remote natural gas fields to produce liquid fuels [2].

The reaction is carried out over supported cobalt-based catalysts at 20–30 bar and at temperatures below 240 °C. The FTS is a highly exothermic reaction due to a standard reaction enthalpy of $-165\ \mathrm{kJ/mol_{CO}}$ combined with CO feed concentrations in excess of 25% and high CO conversions. Furthermore, the FT products distribution is notoriously sensitive to the catalyst temperature. In this regard, an inefficient temperature control would shift the product distribution to lighter hydrocarbons, i.e. methane, which is highly undesired. Accordingly the heat removal from the reactor is a key issue for the development of an intensified reactor technology [3].

Both fixed-bed and slurry reactors are commonly used for the FTS at the industrial scale [3]. In slurry bubble column reactors (SBCRs), the well-mixed liquid phase results in nearly isothermal operation that allows running the process at higher CO conversions per pass. However, catalyst particles for these reactors must be optimized to resist mechanical stress, attrition and hydrothermal effects. An efficient filtration system must be also provided for the separation of the liquid products from the catalyst particles [3,4]. Furthermore, the SBCR technology has a low specific productivity, which makes it convenient only at a very big scale.

The multitubular fixed-bed reactor (MTFBR) configuration is also used at the industrial scale [5], showing advantages like behavior close to plug flow conditions, high catalyst holdup, no need for catalyst separation and less difficult scale-up. However, weaknesses related to mass and heat transfer and pressure drop need to be addressed in view of the process intensification [3,4,6]. Mass transfer limitations may occur since large catalyst particles should be used to limit pressure drop across the catalyst bed [7–13]. The eggshell catalyst configuration may represent a promising solution even if the volumetric active density in the reactor is reduced with respect to the adoption of uniformly impregnated catalyst pellets [7,8].

Concerning the heat removal issue, the dominant pathway of the heat transfer in a MTFBR is associated with the tortuous flow path of the fluid phase. Heat transfer by static thermal conduction in the solid phase is, indeed, insignificant since only contact points are present between the catalyst particles and between the particles and the reactor walls [4]. This results in non-isothermal operation of the reactor with the presence of hot-spots and strong axial and radial T-gradients along the catalyst bed. This, in turn, may lead to a loss of selectivity, to a fast catalyst deactivation and, in the worst case, to the thermal runaway of the reactor [4].

At the industrial scale, such an issue is overcome by limiting the CO conversion per pass and recycling the unconverted syngas as well as a considerable fraction of the liquid reaction products at high flow rates. However, this increases pressure drops and makes the reactor less flexible to be scaled [6].

Nowadays, several research groups are focusing on the development of structured reactors with an improved thermal management suitable for small-scale GTL applications for remote or stranded gas sources [4,6,14–23]. In this regard, microchannel-based FT reactors are now commercially offered by Velocys [24]. The reactor is demonstrated to deliver approximately 175 barrels of FTS products per day [24]. The microchannel-design requires that the catalyst is housed within wave-like fin structures. The pressurized water coolant flowing inside cross-flow microchannels [24] efficiently removes the reaction heat. A major issue of the microchannel system is the fact that it introduces a totally new reactor technology, which is intrinsically more complex and expensive in comparison to the conventional multitubular fixed-bed reactor, a proven workhorse of the chemical and process industry during the last several decades.

As an alternative approach, structured catalysts with different geometries are proposed as viable alternatives for efficient heat removal in MTFBR applications [4,6,14–22]. In this regard, particularly promising results are obtained when the catalytic material is washcoated onto a spatially structured support substrate made of conductive materials [4,6,14–20]. This enables more isothermal operation of the reactor, thus reducing hot spots.

Different metallic supports with different geometries, such as commercial Al-foams and in-house made honeycomb monoliths (composed by alternated flat and corrugated foils) with different cell densities and made of both Fecralloy and Al, were widely studied for the FTS by Montes and coworkers at the University of the Basque Country [4,14,15]. They found that, regardless of the geometry, the adoption of metallic supports enables better performances than the corresponding powdered catalyst. Among the structures, monoliths with high thermal conductivity (made of Al) and high cell density (2300 cpsi) show improved heat exchange capabilities, thus representing a promising alternative to traditional packed-bed reactors [4]. On the contrary, the adoption of washcoated foams seems to be less feasible with respect to the other substrates [19,29]. This is mainly due to the several difficulties encountered during the coating process of the active phase onto these cellular structures. Furthermore, due to their low geometrical surface areas, very thick coatings are required to achieve sufficient catalyst loadings. As a result of the coating process, some catalytic material may be retained, partially blocking the macropores of the foam [14].

The potential of coated conductive monoliths in the FTS was actively investigated also in our group at Politecnico di Milano, Italy [3,6,25]. Visconti et al. [3] demonstrated by numerical simulations the ability of these substrates to manage the heat removal issue of the FTS and to guarantee an excellent temperature control. The heat transfer is strongly enhanced because the primary radial heat exchange mechanism is changed from flow dependent radial mixing in the gas phase associated with the tortuous flow path to static conduction within the thermally connected solid matrix of the honeycomb monolith [3,25], which makes it therefore also independent of the flow rate.

Another alternative concept of catalyst structures with enhanced heat transfer characteristics is represented by the conductive micro-fibrous entrapped catalysts (MFEC) developed by the Tatarchuk group at Auburn University, USA. They consist of sintered micron-sized metal fibers entrapping small catalyst particles [17,18], thus avoiding the need for washcoating. Flow heat transfer experiments demonstrated that MFECs made of conductive metals provided much greater effective thermal conductivities and wall heat transfer coefficients than conventional packed beds of particles. The adoption of MFEC allowed running the FTS at CO conversion levels of 50–80% [17,18].

A micro-structured reactor technology composed by eight parallel catalyst sections sandwiched between metallic cross-flow oil channels for heat exchange was also tested by Myrstad et al. [17] at NTNU, Norway. Each catalyst section was made of two foils with an etched deep pillar structure. The foils were stacked opposite to each other giving 800 μm channel height. The authors showed the capability of this system to efficiently remove the heat generated by a highly active Co-based catalyst working under severe FTS conditions [17].

In view of the development of compact and intensified Fischer–Tropsch reactors, closed cross flow structures (CCFS) packed with catalyst particle were recently proposed by Kapteijn and coworkers at TU Delft [21,22]. CCFSs consist of superimposed inclined corrugated sheets separated by flat sheets. It was numerically shown that the structured flow paths of the fluids through the packing roughly double the overall heat transfer properties of a randomly packed bed reactor. Furthermore, despite of a lower catalyst hold-up, the packed CCFS had a 25% higher C_{5+} productivity per reactor volume than the packed-bed [21,22].