CATALYTIC MULTIPHASE MICROSTRUCTURED REACTORS

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Driven by environmental, safety and economical concerns, chemical industry has been forced, over the past decades, to developed the intensification of its processes. Research in chemical engineering has and continues to play a key-role in this improvement of existing processes and the development of new ones. As far as multiphase reactive processes are concerned, structuring reactors in a multi-scale approach [1] and reducing the characteristic lengths of the limiting physical processes represent a powerful way to achieve process intensification.

Over the past decade, multiphase structured micro-reactors were more and more studied and appear to be promising tools for many applications such as lab tools for intrinsic kinetic studies, auxiliary power units and on-site delocalised production [2]. This attractiveness is mainly driven by low material inventory, compactness, safety, high surface to volume ratio allowing better mass and heat transfers and the ability to reach “new process windows” in chemical synthesis.

At the micro-scale, shorter characteristic lengths lead to a redistribution of the relevant physical processes that govern hydrodynamics: surface tension and viscous forces are often the dominating processes over gravitational and inertial forces. The coupling of these known but non-usual phenomena in traditional reactor design with the reaction represents a new deal that must be put into action by chemical engineers. Today main challenges in the field are hydrodynamics control and characterisation, mass and heat transfer evaluation, scale up issues and, when necessary, solid catalyst coating, loading, re-activation or change-over.

At LGPC, for approximately a decade, We have developed and explored various multiphase contacting concepts based on different physical phenomena at the micro-scale. We have used the so designed micro-reactors for different chemical applications in a wide range of experimental conditions. Below is a non-extensive list of concepts, properties and applications that results from our investigations:

- “Shear-based” micro-mixers generating stable and structured emulsions for homogenous catalysts screening and kinetic data acquisition in G-L and L-L media [3].
- Structured-G-L-interface micro-reactors with grids [4] and pillars [5] that take advantage of the capillary forces with applications for G-L and G-L-S catalysis..
- Single [6] and multichannel [7] continuous falling film micro-reactors (FFMR) displaying a uniform, very stable thin liquid film to conduct catalytic G-L and G-L-S reactions.
- Continuous micro-reactors using segmented flow allowing mass-transfer enhancement and used to investigate new process windows for demanding G-L [8] and G-L-L [9] reactions.

The most recent results concerning the two last items are presented in details. First, the characterisation of mass transfer in a multichannel falling film micro-structured reactor and second, the use of segmented flow to reach new process windows.

Falling film micro-reactor :

A large FFMR from IMM (see figure 1A) with 100 parallel micro-channels (width/depth/length of 600μm/200μm/240mm) has been characterized in terms of mass transfer after checking the hydrodynamics and residence time distribution. Overall G-L-S mass transfer coefficient K_La has been determined using a chemical method: the α-methyl-styrene catalytic hydrogenation to cumene over a thin layer (around 20 μm) of Pd/Al_2O_3 catalyst wash-coated inside the channels (see figure 1B). This reaction is very fast with known intrinsic kinetics [10] allowing to estimate the hydrogen flux transferred from the gas phase to the catalyst surface.

An overall mass transfer coefficient K_La up to 6.5 s^{-1} has been estimated from experiments conducted under pressure(from 3.3 bar to 6.3 bar) and at temperatures ranging between 283 K and 298 K. Such a Kla value is far beyond those obtained for traditional industrial multi-phase reactors (0.1 to 0.5 s^{-1}) and lab-tools reactors (up to 2s^{-1}).

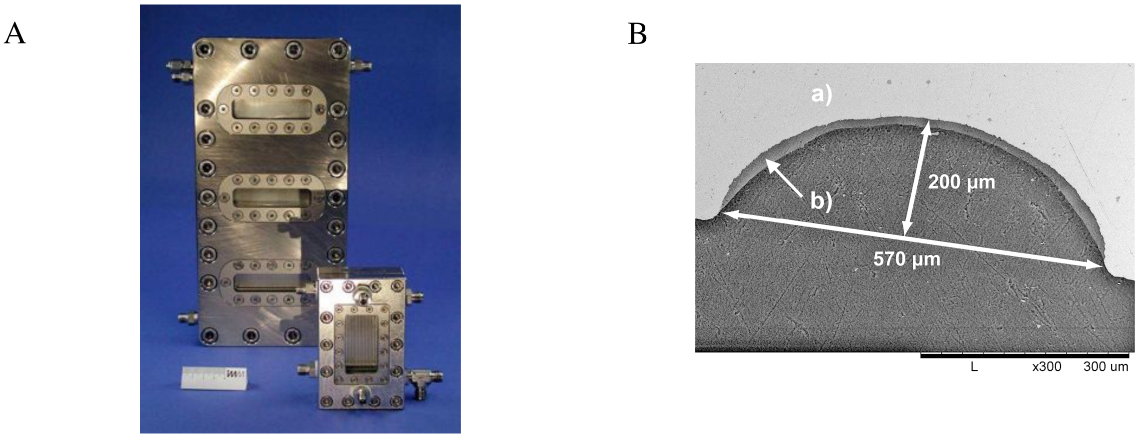
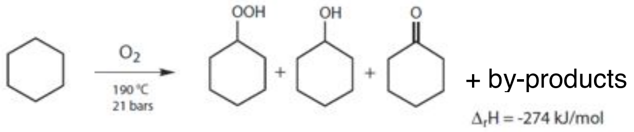


Figure 1: A) Comparison of the Large FFMR with the Standard FFMR; both coming from IMM - B) SEM picture of a channel profile of the large FFMR showing a) the stainless steel plate where channel are etched and b) the coated Pd/Al_2O_3 catalyst layer.

Segmented Flow:

A G-L Taylor flow [11] (figure 2A) has been used to investigate the partial selective oxidation of cyclohexane (equation 3) [8]:



(3)

Industrially, this reaction is performed with a cascade of G-L bubble columns with a limited conversion of 4-5% in order to obtain a selectivity of 75-80% in the desired products. The high exothermicity of this reaction, the cyclohexane volatility and the resulting explosive gaseous mixture are the main constraints that motivates the use of micro-reactor for new process windows investigations.

A silicon chip micro-reactor with a T-junction (figure 2B) was used to perform this reaction with pure oxygen up to 30bar and 200℃. Hydrodynamic studies have been performed in order to understand the bubble formation [5]. The coupling between hydrodynamics and reaction (figure 2C) was studied for 175℃ < T < 200℃ with pure oxygen (green curve) and diluted oxygen, i.e. air (red curve). A smart video monitoring of the gas bubbles shrinking can be used to follow the course of the reaction. For this process, several potential issues for intensification were identified :

- Slightly higher conversions can be achieved with the use of pure O_2.
- An increase in the desired products selectivity is obtained in this reactor with dilute and pure oxygen: 85% < S < 95% likely due to a better control of the temperature and a better mass transfer.
- Clues to perform intrinsically safe operations under concentrations/pressures in the explosive zone with pure oxygen have been identified.

Studies about local G-L mass transfer characterization using physical absorption and image analysis are under progress. Recent results on G-L-L segmented flow will also be presented.

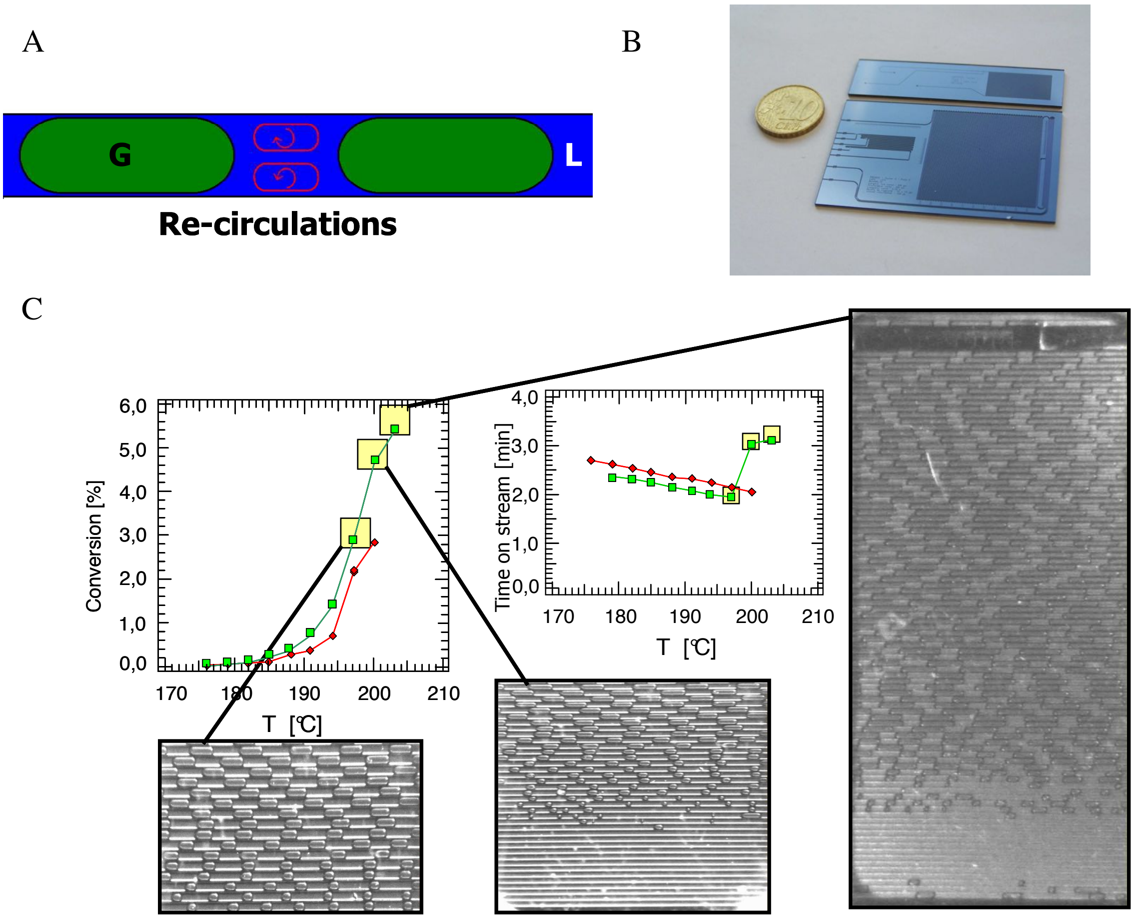


Figure 2: A) schematic representation of the structure of a G-L Taylor flow showing the location of the re-circulations inside the liquid slug - B) Silicon chip reactor used in this study - C) experimental results showing the coupling between reaction, time on stream and gas consumption.

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