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Modelling and simulations of a monolith reactor for three-phase hydrogenation reactions — Rules and recommendations for mass transfer analysis

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ABSTRACT

A strategy for the scale-up of a monolith reactor dedicated to gas-liquid catalytic reactions is worked out; focus is made on the crucial step of gas-liquid mass transfer modelling via a steady-state numerical study based on a single channel and single unit cell representation, using a frame moving with the bubble and solving the liquid phase only. The relevance of this simplified approach is assessed through a specific case (given bubble shape, channel diameter and fluid flow rates), and hydrodynamics as well as mass transfer results are successfully compared to previously published numerical, semi-analytical and experimental works. Influence of unit cell length and of catalytic surface reaction rate is thoroughly investigated. Inferred overall mass transfer coefficients are found to increase with bubble frequency, due to higher interfacial area in unit cell and intensified recirculation in slug. Film contribution to mass transfer is usually found dominant in the case of short bubbles with reactive wall, and hardly varies with reaction rate. However, this contribution is strongly linked to bubble frequency, and a reliable evaluation of local mass transfer by correlations demands accurate knowledge on the precise dimensions of bubble, slug and film entities.

1. Introduction

Chemicals and fuels are produced through catalytic gas-liquid-solid reactions in a wide range of industries, including petrochemicals, fine chemicals, pharmaceuticals and biochemicals. Conventional technologies to host such gas-liquid-solid reactions are fixed-bed, slurry bubble column and fluidized-bed reactors. Slurry bubble column reactors, and fluidized beds to a lesser extent, combine three major advantages: the possibility for continuous catalyst replacement, a much reduced intra-particular diffusion path length (due to the small size of catalyst particles), and a good heat transfer efficiency. However, they suffer from some drawbacks such as liquid back-mixing, significant attrition of the catalyst and need for catalyst separation and recycling. On the other hand, despite fixed-bed reactors can be operated closer to plug flow with negligible attrition of catalyst, restrictions quickly emerge regarding soaring pressure drops which ultimately force a use of large (millimetric) particles which unavoidably imply significant internal diffusional limitations. In addition, the traditional cocurrent downward configuration (trickle-bed reactors) can give rise to maldistribution of the liquid resulting in catalyst partial wetting at low flow rates which render such reactors prone to hot spots inception, thus catalyst deactivation and even thermal runaway [1]. Another difficulty encountered with conventional multiphase reactors is their scale-up to industrial size units. Although these conventional reactors still play a major role in industrial processes, researchers strive looking for advantageous alternative technologies.

Structured reactors have been claimed over the past several years to offer interesting possibilities; among them, Monolith Reactors (MRs), also called ‘honeycomb reactors’, have been considerably studied for almost four decades as they represent a promising cutting-edge technology to circumvent the above mentioned problems enumerated in the case of conventional reactors. MRs were initially developed as catalytic converters for the automotive industry; they have been extended to include other environmental applications such as selective reductions (DeNOx catalysts) used in power plants and incinerators [2]. More recently, MRs have emerged as promising candidates competing with conventional gas-liquid-solid reactors, as they offer several advan-

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Nomenclature

a	Bubble interfacial area; ($m^2{}_B\,m^{-3}{}_{UC}$)
c	Concentration of dissolved gas; ($mol\,m^{-3}{}_L$)
$c_{overall}$	Volume averaged concentration, as defined in Eq. (6); ($mol\,m^{-3}{}_L$)
$c_{s,mean}$	Average slug concentration; ($mol\,m^{-3}{}_L$)
c_{wall}	Wall concentration; ($mol\,m^{-3}{}_L$)
c^*	Dissolved concentration at saturation; ($mol\,m^{-3}{}_L$)
D	Molecular diffusion of dissolved gas in the liquid phase; ($m^2\,s^{-1}$)
d_B	Bubble diameter; (m)
d_c	Channel diameter; (m)
dS	Elementary bubble surface; ($m^2{}_B$)
dV	Elementary volume; (m^3)
$\mathbf{g}$	Gravity acceleration vector; ($m\,s^{-2}$)
K_C	Rate constant of first order surface reaction; ($m^3{}_L\,m^{-2}{}_{wall}\,s^{-1}$)
k_La	Volumetric mass transfer coefficient; ($m^3{}_L\,m^{-3}{}_{UC}\,s^{-1}$)
L_{UC}	Unit cell length; (m)
L_f	Liquid film length; (m)
MR	Monolith reactor
N	Gas molar flux, as defined in Eq. (5); ($mol\,s^{-1}$)
$\mathbf{n}$	Normal vector; (–)
P	Pressure; (Pa)
ΔP	Pressure drop; (Pa)
Q_L	Volumetric flow rate; ($m^3\,s^{-1}$)
r	Radial coordinate; (m)
R_B	Bubble radius; (m)
U_B	Velocity of bubble center of mass; ($m\,s^{-1}$)
U_{TP}	Two-phase velocity, $u_{Gs}+u_{Ls}$; ($m\,s^{-1}$)
$\mathbf{u}$	Velocity vector; ($m\,s^{-1}$)
u_{Gs}	Superficial gas velocity; ($m\,s^{-1}$)
u_{Ls}	Superficial liquid velocity; ($m\,s^{-1}$)
u_{zG}	Axial component of gas velocity; ($m\,s^{-1}$)
u_{zL}	Axial component of liquid velocity; ($m\,s^{-1}$)
V_L	Liquid volume; ($m^3{}_L$)
V_{UC}	Unit cell volume; ($m^3{}_{UC}$)
z	Axial coordinate; (m)

Greek symbols

ε_G	Gas hold-up; (–)
δ_f	Film thickness; (m)
μ_G	Gas dynamic viscosity; (Pa s)
μ_L	Liquid dynamic viscosity; (Pa s)
ρ_L	Liquid density; ($kg\,m^{-3}$)
σ	Surface tension; ($N\,m^{-1}$)

Dimensionless Groups

Ca	Capillary number, $\frac{\mu_L U_B}{\sigma}$; (–)
Re	Reynolds number, $\frac{\rho_L U_B d_c}{\mu_L}$; (–)
Re_G	Superficial gas Reynolds number, $\frac{\rho_G u_{Gs} d_c}{\mu_G}$; (–)
Re_L	Superficial liquid Reynolds number, $\frac{\rho_L u_{Ls} d_c}{\mu_L}$; (–)
Sc_L	Liquid Schmidt number, $\frac{\mu_L}{\rho_L D}$; (–)
Sh_L	Liquid Sherwood number, $\frac{k_L d_c}{D}$; (–)

tages, e.g., the catalytic layer deposited on the wall of the numerous MR channels is thin enough (ca. 10 μm) to minimize internal diffusional resistances; the channels host specifically tunable gas-liquid flow regimes (chief among them the so-called Taylor or train bubble or slug flow), which can prove particularly convenient in terms of mass transfer interfacial area; pressure drop in MR is low; fluids flow freely avoiding reactor fouling and clogging and limiting the occurrence of hot spots; MRs offer the opportunity to perform efficient reaction heat removal through the monolith backbone provided that it is built in highly heat-conducting material.

Many works have been dedicated to the study of MR operation where the literature reports experimental studies of fluid distribution into the channels of monolith blocks [3–6], flow regimes inside the channels [7–10], and mass transfer between gas and liquid phases over the entire apparatus [11,12]. The overall volumetric gas-liquid mass transfer coefficient, k_La, was reported to be much larger in MR operating in the Taylor flow regime (0.1–1 s^{-1}) [11,13,14] than in stirred tanks (0.03-0.4 s^{-1}), bubble columns (0.005–0.25 s^{-1}) or packed beds (0.004–1 s^{-1}) [15]. This enhanced mass transfer was attributed to the existence of a thin liquid film (a few tens of μm) between the bubble and the channel wall, as well as to the efficient convective mixing within the liquid slugs provided they are short enough [16]. Of practical interest, it was shown that k_La values measured in MR correlate rather well with those predicted from single-channel models [11,14]. Indeed, most of the experimental and theoretical works on gas-liquid mass transfer have been devoted to single millimetric capillaries [12,16–23]. The relative contributions of bubble caps and lubricating film to the gas-liquid mass transfer were discussed more specifically, though the conclusions were mainly drawn for non-reactive systems where likelihood of film saturation with the transferring species drastically jeopardizes such level of discrimination. In such a situation, transfer through bubble caps becomes the only effective pathway turning k_La insensitive to bubble length or channel diameter as observed by Berčič and Pintar [18]. Conversely, for short unit cells (bubble + slug lengths <50 mm) and bubble velocities >0.15 $m\,s^{-1}$, simulations from van Baten and Krishna [19] showed that scalar transport through the film accounts for 60–80% of the overall k_La values. Experimental results of Vandu et al. [12] also confirmed a dominant film contribution for unit cells lower than 25 mm. This latter scenario becomes especially crucial when a heterogeneous reaction occurs at the catalyst coated wall due the generated concentration gradient, and in this case the proposed chemical engineering models often neglect (with varying degrees of success) the possible interaction between the different transfer pathways [24–26].

One of the rare and complete examples of a development strategy of a MR was illustrated by Haakana et al. [27] who took lactose oxidation as a study case. They used several different mockup experiments to study separately different phenomena, e.g., hydrodynamics, mass transfer and intrinsic kinetics, and ultimately, the different sub-models were combined for a complete mathematical description. Except this relatively detailed study, a methodology for scale-up or design of a MR apparatus accounting for local inter-channel disparities of the hydrodynamics and concentrations stemming from unequal flow distribution in the parallel channels is rarely proposed.

In the present work, a strategy for modelling a MR as a whole is described. The objective is to develop a pre-design tool for industrial-scale reactors applied to highly exothermal reactions. Ascending Taylor flow is assumed in the channels, and a model reaction rate is considered to occur at channel walls. The chosen strategy allows focusing on gas-liquid mass transfer as part and parcel of the entire mass transport mechanisms in the unit cells as a key-point for MR performance. Thus these phenomena are specifically modelled and simulated by means of Computational Fluid Dynamics. For a given set of operating parameters (i.e., fixed gas and liquid flow rates), the overall and local mass transfer rates are quantified and discussed for various values of unit cell length and reaction rate.