

Single Pellet String Reactor for Intensification of Catalyst Testing in Gas/Liquid/Solid Configuration

A.I. Hipolito¹, M. Rolland¹, C. Boyer¹ and C. de Bellefon²

¹ IFP Energies nouvelles-Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize - France

² Laboratoire de Génie des Procédés Catalytiques, CNRS-CPE, BP 2077, 69616 Villeurbanne Cedex - France

e-mail: ana-isabel.fernandes-hipolito@ifpenergiesnouvelles.fr - mathieu.rolland@ifpenergiesnouvelles.fr
christophe.boyer@ifpenergiesnouvelles.fr - cdb@gpc.cpe.fr

Résumé — Réacteur catalytique de type “filare” pour l’intensification de tests catalytiques en configuration gaz/liquide/solide — L’optimisation du catalyseur est une étape clé pour l’optimisation d’un procédé catalytique du point de vue des rendements, de l’efficacité énergétique et de la sélectivité des réactions. La stratégie de développement d’un catalyseur comprend des tests effectués sur des réacteurs pilotes avec des charges réelles ou modèles. Cette étape a fait l’objet de nombreuses études ces dernières décennies portant sur le dimensionnement des réacteurs, l’amélioration des outils d’analyses et les procédures opératoires. La plupart des études ont pour but de déterminer l’activité catalytique de catalyseur sous forme de grain dans des conditions isothermes de façon à pouvoir déterminer les paramètres cinétiques de la réaction. Avec l’optimisation des catalyseurs, les flux de transfert de matières externes aux grains peuvent devenir l’étape limitante, dans les réacteurs de laboratoire standard, par rapport aux flux de réaction. Ce problème est particulièrement critique pour les réactions rapides et très exothermiques. Une nouvelle géométrie de réacteur est proposée pour intensifier les transferts de matières autour des grains de catalyseur et accélérer les vitesses superficielles des fluides : le “réacteur filaire”. Pour caractériser cette nouvelle géométrie de réacteur, une étude hydrodynamique a été menée avec un réacteur filaire horizontal de section carrée de $4,0 \times 4,0 \text{ mm}^2$ rempli de particules sphériques de diamètre compris entre 2 et 4 mm et simulant des grains de catalyseur. Les régimes d’écoulement ont été étudiés à partir d’analyses d’images, des mesures de perte de pression et de distribution de temps de séjour qui ont été effectuées en écoulement monophasique liquide et diphasique gaz/liquide. Deux principaux régimes d’écoulements ont été observés : un régime de “bulles isolées” et un régime de type “stratifié”. Les rétentions liquides sont toujours supérieures à 60 %, ce qui indique en complément d’observations visuelles que le catalyseur est toujours correctement irrigué par l’écoulement liquide. En écoulement diphasique gaz/liquide, l’écoulement est de type piston puisque les nombres de Peclet sont toujours supérieurs à 40. La perte de pression est principalement contrôlée par les forces de frottement liquide/solide et les valeurs de perte de pression restent très faibles en conditions de tests catalytiques ($< 0,1 \text{ bar}$). Les caractéristiques hydrodynamiques indiquent donc que ce réacteur est approprié pour des tests catalytiques. Enfin, ce type de réacteur a été mis en œuvre en conditions de réactions catalytiques pour effectuer des tests d’un catalyseur commercial pour une réaction d’hydrogénation de l’allène. Le réacteur a permis d’effectuer des tests en conditions isothermes avec une très faible quantité de catalyseur (inférieure à 2 cc) et d’accéder aux performances catalytiques pour des temps de contact très courts impossible à atteindre avec des réacteurs à lits fixes conventionnels dans de bonnes conditions hydrodynamiques. Pour un même temps de séjour, la conversion en allène ne varie pas, ni avec la pression opératoire, ni avec le débit de charge, ce qui confirme que ce type de réacteur permet d’effectuer des tests catalytiques avec des réactions rapides sans limitation aux transferts de matières externes aux grains.

Abstract – Single Pellet String Reactor for Intensification of Catalyst Testing in Gas/Liquid/Solid Configuration – Catalyst improvement is a key route toward process improvement in terms of yield, energy efficiency and selectivity optimization. The catalyst development strategy includes catalyst testing on a model or real feedstock. This key step has been the focus of many studies during the last decades concerning reactor design, analytical tool development and operating procedures. Most studies aim to determine catalytic grain activity in isothermal conditions so as to be able to understand and predict the kinetics. With catalyst improvement, in the lab-scale reactors available, the mass transfer rate can become the limiting step compared with the reaction rate, especially for fast exothermic reactions. A new reactor geometry is proposed to intensify the mass transfer and to accelerate the fluid superficial velocities: the single pellet string reactor. To characterize this new geometry, a hydrodynamic study was carried out in a horizontal single pellet string reactor with a $4.0 \times 4.0 \text{ mm}^2$ square section, filled with spherical particles of diameter varying between 2.0 and 4.0 mm. In this hydrodynamic study, visual observations of the flow patterns were performed, as well as pressure drop measurements and residence time distribution analysis in single liquid phase flow and two-phase flows. In every configuration tested, two main regimes were identified: the “isolated bubbles” regime and the “stratified” regime. Peclet number and liquid hold-up were deduced from the residence time distribution analysis. The measured liquid hold-ups are always higher than 0.6, which indicates, in addition to the visual observations and colorimetric tests, that the catalyst is always fully wetted by the liquid film. The axial dispersion measurements showed that the single liquid phase flow cannot be interpreted by a classical axial dispersion model. However, when a gas phase is added, the flow becomes closer to plug flow, with Peclet numbers always higher than 40. It has been shown that the pressure drop is controlled by the liquid/solid friction surface and that the pressure drop is not a limiting parameter in the reactor’s operation (values always lower than 0.1 bar). So, from a hydrodynamic point of view, this new reactor exhibits characteristics suitable for its use in catalytic tests. Finally, this reactor was implemented under reaction conditions to study hydrogenation reactions with a real industrial catalyst. The selective hydrogenation of allene was studied. The string reactor was shown to run isothermal kinetic tests with a very small amount of industrial-sized catalyst particles (less than 2 cc) and to explore kinetics of fast reaction at high space velocities impossible to achieve in standard fixed bed units with appropriate hydrodynamic conditions. For constant residence time, the allene conversion does not vary with pressure and feed flow rate, which confirms that the string reactor allows one to perform catalytic tests with such a fast reaction without external mass transfer resistance.

NOTATION

D_{ax}	Axial dispersion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$)
d_p	Particle diameter (mm)
D_R	Reactor diameter (mm)
L	Reactor length (m)
LHSV	Liquid Hourly Space Velocity
Q_L	Liquid volumetric flow rate ($\text{L} \cdot \text{h}^{-1}$)
Pe	Peclet number $\left(Pe = \frac{u_L \cdot L}{D_{ax}} \right)$
S_{wetted}	Total wetted surface (walls and particles) (m^2)
u_s	Superficial velocity ($\text{m} \cdot \text{s}^{-1}$)
u_{Ls}	Superficial liquid velocity ($\text{m} \cdot \text{s}^{-1}$)

u_{Gs}	Superficial gas velocity ($\text{m} \cdot \text{s}^{-1}$)
V_{void}	Void volume (m^3)

Greek Letter

β_L	Liquid hold-up
ΔP	Pressure drop (mbar)
ε	Bed porosity
μ	Viscosity (Pa.s)
ρ	Density ($\text{kg} \cdot \text{m}^{-3}$)

Subscript

G	Gas
L	Liquid

INTRODUCTION

Chemical Industry: Toward Sustainable Process Design

The traditional trend in the chemical industry has always been toward more economical processes. More active, longer lasting catalysts have thus been the golden route toward plant improvement over the decades.

Since the 70s, energy prices have increased and volatility has led to a demand for drastic improvement of processes regarding energy efficiency. New technologies and designs have quickly been accepted due to the economic advantages of cutting costs. Energy and process efficiency improvements are now additionally driven by a will to reduce CO₂ emissions. Energy optimization is achieved through a decrease in the temperature required to run key equipment processes and better thermal integration through energy studies, for example. More active catalysts or improved technologies for distillation and separations are particularly interesting.

There is an incentive for optimized plant design both at the process level and at the equipment level. An improved capability to predict equipment performances, for example a reactor, is quite an advantage for a process licensor as he can reduce over-design not only on this reactor (size, catalyst inventory, etc.) but on the whole plant (recycle loop, hydrogen production plant, purification plants, etc.).

Concerning the catalyst section design, the scale-up is sometimes difficult since some reactions prove to be difficult to handle on a small scale. This is the case of fast reactions, such as selective hydrogenation, where small-scale testing induces mass transfer resistance from the feedstock to the catalyst grains that may mask the real performance of the catalyst on an industrial scale. In these cases, improved design requires the development of innovative catalyst testing tools.

Another important driver in the chemical industry is the need for higher purity products. Higher purity products when used as feedstock lead to improved process performance, and reduce pollution. For example, a 0.1% purity increase in paraxylene directly translated to fewer defects in the Nylon fibres manufactured from it, and thus less breakage during winding. Decreasing the diesel sulfur content from 50 ppm to 10 ppm in 2009 requires new generations of desulfurizing catalysts with 99.9+% conversions, whose development has been challenging regarding catalyst testing and product analyzing.

To summarize, sustainable process development is bringing new incentives to improve catalyst performances (yield and selectivity) and catalyst testing abilities, through more severe product specification requiring improved testing tools, through a need for a more accurate understanding of catalytic reactions and through a more integrated process design (Fig. 1).

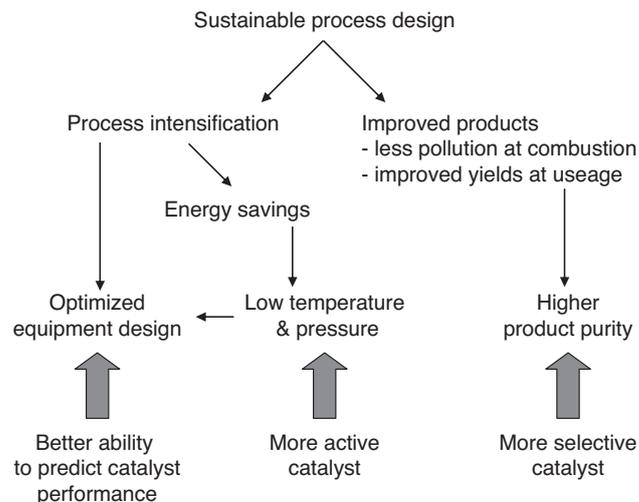


Figure 1

Sustainable process design and catalyst development.

Industrial Catalyst Development and Testing

The catalyst development strategy includes designing and manufacturing catalysts, and catalyst evaluation on simulated or real feedstock. Catalyst testing is a key step and has been the focus of many studies during the last decades concerning reactor design, analytical tool development and operating procedures.

Academic kinetic studies try to determine the isothermal intrinsic kinetic of a catalyst on the catalytic site scale and describe it using adsorption and chemical reaction laws. Catalytic sites have to be supported on a medium that fulfils the process constraints. In the chemical industry, support is often catalyst pellets made out of a solid matrix presenting suitable mechanical strength, porosity and physico-chemical properties such as acidity to enhance the catalytic processes. A recent trend in solid support technology has been the use of coated channels bundled in monoliths: these are mostly used for low pressure gas treatment such as combustion engine exhaust converters, power plant fumes' post-treatment and hydrogen production processes. The present study mainly focuses on the testing of industrial catalysts supported on pellets of spherical shape.

The grain kinetic, that is the apparent kinetic measured on a pellet scale, can be significantly slower than the intrinsic kinetic (on the site scale). The difference can be explained by internal diffusion limitations, incomplete wetting and side effects due to the use of real feedstock such as catalyst fouling, pore blockage by large molecules, etc. Catalyst pellet apparent kinetic and intrinsic kinetic measurements require that there is no external mass transfer resistance; that is that the molecular flux is supplied to the particle or the active site

at a rate faster than it is consumed by the reaction, and similarly that products are removed fast enough not to hinder the reaction performances. The external transfer rates depend greatly on the hydrodynamic flow near the pellets or the active sites. As a rule of thumb, in fixed bed reactors, external transfer rates increase with superficial velocities to the power $2/3$. The reactor hydrodynamic is thus quite important to consider when collecting kinetic data. Using models, it is theoretically possible to account for external transfer limitations and derive the pellet or intrinsic kinetics of a catalyst from kinetic data measured in the presence of limitations. These models can then be integrated in a reactor model in order to predict the industrial reactor performances (Fig. 2). However, to achieve a good accuracy in the derived kinetic, external transfer rates should be of the same order of magnitude as the kinetic consumption and production rates. If a reaction is 10 times faster than the mass transfers, then the apparent measurement will be the transfer rate with little influence of the reaction kinetic: every test catalyst will then give the same results and only a lower bound for the catalyst activity can be determined from the experimental data.

As seen in Figure 2, it is obvious that the industrial performance can be predicted once the catalyst apparent kinetic is determined. This explains why, in the last step of catalyst development, catalyst testing is generally performed on industrial pellet size: extrudates or spheres. Some tests are, however, performed on crushed catalyst particles to evaluate the catalyst efficiency in order to optimize the catalyst formulation, shape and size if the catalyst apparent activity is strongly limited by internal diffusion.

Furthermore, it is straightforward to understand that if the reactor hydrodynamic behavior is identical for both the industrial and pilot units, the experimental data measured on the catalyst particle scale can be directly used to predict the industrial unit performances, as they are identical. This is the fundamental reason why in the industry, most catalysts are tested in a pilot unit using the same reactor technology (from the hydrodynamic point of view) as the industrial units (fixed beds, slurry bubble columns, batch reactors). Testing on the

same technology also makes it easier to validate material, equipment and procedures, and thus convince the customer.

Even with the same reactor technology, the hydrodynamic in the pilot unit and industrial reactor may be quite different for various reasons. The first reason for hydrodynamic difference is that catalysts are tested by keeping the “reaction time” identical to those on an industrial scale, more exactly by keeping the LHSV (Liquid Hourly Space Velocity) constant. The LHSV is defined as the ratio of the liquid flow rate to reactor volume. In a cylindrical reactor, the feedstock must flow through the whole catalyst bed height in the same amount of time in the industrial reactor (about 5-10 m high) and in the pilot plant, tenfold shorter (0.1-0.5 m high). Therefore, superficial velocities are between 10 and 100 times lower in the pilot unit. This leads to a drastic reduction in external mass transfer rates, which may be limiting in the pilot unit and not in the industrial reactor. When downscaling fixed bed reactors, different flow patterns exist near the reactor wall (more void volume) and in the center of the reactor. In a 3 m diameter industrial reactor, these wall effects are negligible, whereas in a 15-mm diameter reactor, they may have quite negative effects on the reactor performance. Some criteria have been derived to ensure correct operation, such as minimal length [1, 2] and a reactor to particle diameter ratio larger than 15-20 [3]. Thermal management of the unit can also be of major importance. Catalysts are preferentially tested in isothermal mode to properly access kinetic parameters. Most reactions do produce or consume heat so that an isothermal operation requires extracting or providing heat. For quite exothermic reactions, this is critical as an increase in temperature leads to an increase in the catalyst activity, and hence more heat is produced. For some specific sets of conditions, thermal instabilities can lead to the loss of control of the reactor [See the paper of J.M. Schweitzer and C. Lopes Garcia in the same issue].

Scalability of experimental data is becoming more of an issue as there is a demanding trend for reducing pilot unit sizes for several reasons: lower inventory of hazardous products, lower investment and operating costs, faster reaction

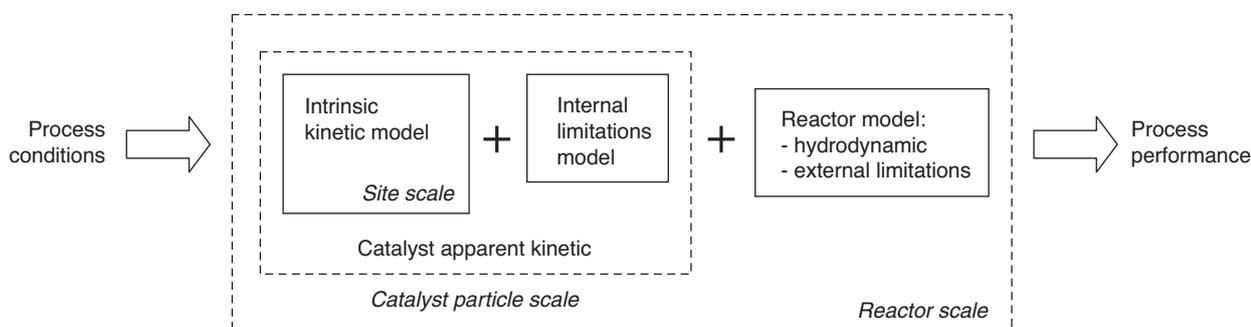


Figure 2

Process performance modelling.

time, more units per building surface area, longer lasting reference feedstocks, etc. Reducing a reactor size brings up new challenges regarding its design, as discussed previously, and chemical engineering technology innovations are the only way forward. For example, in the 90s, the introduction of inert, small-sized (100 μm) particles in between the catalyst made it possible to test in 10-20-mm diameter reactors [4, 5].

Catalyst development and industrial plant performance prediction is a complex process that includes experimental and modeling work. When suitable, it is possible to simplify the modeling work by testing industrial-sized catalyst particles with a reactor technology identical to the industrial one. In the cases of “slow”, not too exothermic reactions, this is generally feasible. In the next paragraph, we will focus on the specific case of fast and exothermic reactions where traditional catalyst testing tools are not suitable even with a model.

Fast Exothermic Reactions

Fast reactions are defined here as reactions where the kinetic is faster than the external mass transfer in conventional small-scale reactors. This is, for example, the case of the hydrogenation of α -methylstyrene (AMS), which is so fast that it is commonly used to measure the rate of H_2 dissolution in hydrocarbons in fixed bed reactors [6, 7]. These reactions are generally very exothermic (100 to 200 kJ/mol) and a careful heat management design must be used to ensure that the reactor is isothermal in both radial and axial directions.

There are small lab-scale tools available to perform kinetic tests on these reactions. The Robinson-Mahoney reactor is the most commonly quoted [8]. It consists of a batch vessel in which is inserted an annular basket containing the catalyst pellets. Gas is continuously flowing in the vessel along its axis and a stirrer creates a circulation of the liquid/gas mixture through the basket. This system produces high velocities in the particle bed, enhancing external mass transfers. The main drawback of this system is that the mass transfer enhancement is difficult to evaluate and depends on many factors: basket positioning, stirrer shape and rotation speed, and more annoyingly, on the particle arrangement inside the basket. Flow and mass transfer in a basket filled with extrudates or spheres will be quite different. This is the reason why this kind of reactor is most frequently used with crushed and sieved catalysts. Nevertheless, in this case external mass transfer limitations may still occur since the catalyst is even more active and a model is necessary to predict apparent catalyst particles. In order to find other ways to test catalysts of fast and exothermic reactions, a new kind of pilot plant reactor was evaluated, the single pellet string reactor.

Single Pellet String Reactor

A new concept of the fixed bed reactor is proposed to determine the kinetic on fast exothermic reactions. In this

geometry, the reactor diameter is close to the particle diameter. As the reactor section is small, even for low flow rates, it is possible to operate with velocities similar to those of the industrial scale for a similar amount of catalyst as in a standard pilot plant (Tab. 1). In these conditions, it is expected that heat and mass transfer would be as fast as in industrial reactors or even faster. Numerous studies have indeed shown that in empty tubes of a few millimeters in diameter, mass transfer between phases was greatly enhanced because of the segmented flow (Taylor flow), resulting in thin films between the bubbles/droplets and the walls. It is expected that in the presence of a catalyst particle, the two-phase flow will exhibit similar heat and mass transfer enhancement.

TABLE 1

Comparison of superficial velocities in industrial and pilot unit reactors

	Industrial reactor	Standard fixed bed pilot unit	String pellet reactor
LHSV (h^{-1})	1 to 20		
u_{Ls} (mm/s)	1-100	0.03-3	1-100
u_{Gs} (mm/s)	10-200	0.5-10	10-200

As the wall surface to volume ratio is much higher than in traditional fixed beds, heat management is easier: a more isothermal operation is expected. Wall effects will have an impact on the hydrodynamic that need to be assessed; however, it is expected that all particles will be in close contact with the same gas and liquid flow so that the chemical reactions should be occurring in the same manner for all the particles. There is no longer any difference between pellets close to or far from the wall since they are all near the wall.

The single pellet string reactor has been used by several authors to measure the intraparticle diffusion coefficients [9, 10] and the tortuosity coefficients [11, 12] in solid catalysts. The intrinsic kinetic parameters for steam reforming of n -heptane [13] and for olefin hydrogenation [14] were also measured in this type of reactor. Regarding hydrodynamics, Lee *et al.* [15] measured the pressure drop and the axial dispersion in a cylindrical string reactor. They proposed a modified Ergun correlation for the pressure drop and an empirical correlation for the Peclet number. All the studies cited above were performed with single-phase systems (liquid or gas).

More recently, Kallinikos and Papayannakos [16, 17] have performed two studies in gas/liquid/solid systems using string reactors in a spiral shape. In their first study [16], they conducted hydrodesulfurization of diesel in three different spiral reactors to study the influence of the reactor's length. They concluded that the reactor's performance is independent of the liquid superficial velocity and of the reactor's length in the range 2 to 6 m. In their second study [17], four

spiral reactors were filled with non-porous cylindrical particles. They measured the influence of the ratio of particle diameter to reactor diameter (d_p/D_R) and of the reactor's length on the pressure drop and axial dispersion (Peclet number). One conclusion of their study is that a governing parameter is the ratio of gas to liquid superficial velocities (u_{G_s}/u_{L_s}). From the experimental results and using simple power equations, Kallinikos and Papayannakos [17] proposed fitting correlations for pressure drop and Peclet number.

Single pellet string reactors present quite complex hydrodynamic patterns that cannot yet be explained with simple physical models. In the following paragraphs, the results of a hydrodynamic study in this reactor geometry with a square cross-section channel are presented, as well as its performances for allene hydrogenation.

1 SINGLE PELLET STRING REACTOR HYDRODYNAMICS

The hydrodynamic of a linear horizontal square-shaped single pellet string reactor was studied in single liquid phase flow and two-phase flow. The liquid Residence Time Distributions (RTD) and the pressure drop were measured and analyzed in order to characterize the hydrodynamic of a single pellet string reactor.

1.1 Experiment Description

This study was carried out in a horizontal PMMA reactor with a square cross-section of $4 \times 4 \text{ mm}^2$ filled with glass spherical particles. The reactor was operated at ambient temperature and atmospheric pressure. The fluids used were *n*-heptane and nitrogen. The volumetric liquid flow rates were in the range of 0.02 L/h to 3.0 L/h and the volumetric gas flow rates were between 0.1 L/h and 50.0 L/h. In the two-phase flow experiments, the gas flow is injected into the liquid flow line in order to achieve steady two-phase flow before the reactor's inlet. For each set of operating conditions, flow regime observations (videos), liquid residence time distribution measurements and pressure drop measurements were performed. The effect of the d_p/D_R ratio was studied by measuring the hydrodynamic parameters cited previously with glass spheres of 2.0, 3.0 and 4.0 mm diameter (see Tab. 2). A complementary qualitative study of the wetting was performed using porous alumina beads.

Residence time distribution curves were obtained by monitoring the concentration profiles of a tracer (isohexadecane) at the inlet and outlet of the reactor using two local optical probes that measure the refractive index of the liquid inside the flow. The refractive index is converted into a tracer mass fraction using a calibration curve. The tracer pulse is

injected once the reactor reaches a steady-state operation, identified when pressure fluctuations are cyclic.

The geometric characteristics and the bed porosity (ϵ) of each configuration are summarized in Table 2.

TABLE 2

Geometric characteristics and bed porosity of each configuration tested

Configuration	HR1	HR2	HR3
d_p (mm)	2.0	3.0	4.0
d_p/D_R	0.5	0.75	1.0
ϵ	0.48	0.63	0.48

1.2 Flow Structure

In Figures 3 and 4 the particle arrangements in the channel for the three configurations tested are represented, schematically (side and section views, respectively). In the HR1 configuration (Fig. 3, 4a), the particles are arranged more or less randomly but they form a compact system. The liquid flows mainly at the bottom of the channel but also in the upper corners of the channel. The gas flows at the top and in the center of the channel, around the particles. This configuration is, among the three configurations tested, the closest to a fixed bed due to its higher tortuosity.

In the HR2 configuration, the particles are arranged mostly as shown in Figures 3 and 4b, the rest of the particles being aligned (Fig. 3, 4d). This system is compact but it is not at its maximum compactness. Gas flows preferentially at the top of the channel except when there is a particle that blocks the passage. In this last case, the gas bubbles go under and around the obstacle and immediately back to the upper part of the channel. The liquid phase is thus observed in the bottom part of the channel and as a film in the upper corners of the channel.

For the configuration HR3, the spheres are aligned, leaving only the corners for gas and liquid flow (Fig. 3, 4c). The gas flows only in the upper corners of the channel on both sides of the top of the spheres. Liquid is observed in the bottom part of the channel as well as a film in the upper corners.

For the three cases studied in this work, two major regimes were identified as a function of the ratio of gas to liquid superficial velocities (u_{G_s}/u_{L_s}). For high u_{G_s}/u_{L_s} ratios (≥ 10), the gas phase was flowing at the top of the reactor (and in the center in HR1) with some liquid slugs with varying length between the long gas slugs. This flow pattern was defined as "stratified" flow. For low u_{G_s}/u_{L_s} ratios (< 10), most of the top space was filled with liquid, with some bubbles passing through the reactor. We define this flow pattern as "isolated bubbles" flow. In both flow patterns, the glass spheres appear to be constantly wetted.

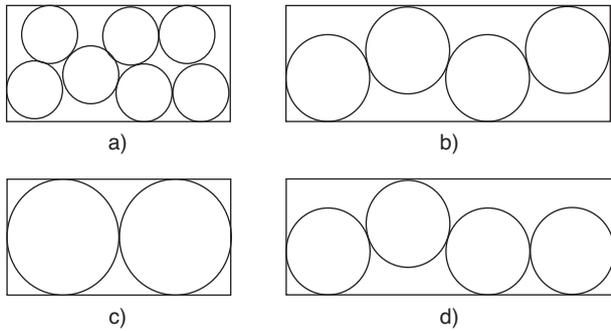


Figure 3
Representation of the particle arrangements in the channel (side view): a) HR1; b) and d) HR2; c) HR3.

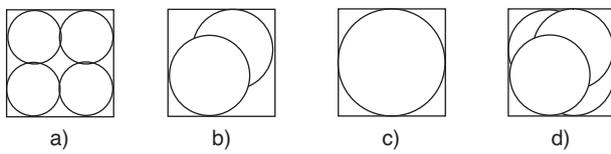


Figure 4
Representation of the particle arrangements in the channel (section view): a) HR1; b) and d) HR2; c) HR3.

and outlet. At low flow rates, the inlet signal presents a large tail and some slope changes (Fig. 5a), which may indicate the existence of some recirculation zones in the pipe between the injection point and the optical probe at the reactor’s inlet. When the liquid flow rate increases, the inlet signal becomes closer to a Dirac pulse (Fig. 5b, c). These results are similar to those obtained in the HR1 and HR2 configurations which are presented in Hipolito *et al.* [18]. As the shape of the inlet signal depends on the liquid flow rate, it is necessary to use a numerical model to correctly interpret the outlet signals.

For each experiment, a classical axial dispersion model was applied to the inlet signal in order to simulate an outlet signal that was compared with the outlet experimental signal. An example of the model results is presented in Figure 6 for a liquid flow rate of 0.5 L/h in the HR2 configuration. In this case, as well as for all liquid flow rates in the three configurations, the model does not describe the experimental results correctly, whatever the Peclet number.

In all the configurations tested, the flow hydrodynamic in single liquid phase flow is quite complex and cannot be interpreted with a classical axial dispersion model. For low liquid velocities, the characteristic diffusion time in a liquid strip of 1 mm is of the same order of magnitude as the liquid residence time in the reactor. So, the radial diffusion has a disturbing effect on the tracer convection and consequently, on the axial dispersion. This hypothesis was confirmed by CFD simulations that are detailed in Hipolito *et al.* [18] and in which some stagnant zones were identified. The tracer diffusion from the stagnant zones to the main stream line explains the long tails obtained in the outlet concentration profile.

1.3 RTD Results

1.3.1 Single Liquid Phase Flow Results

In Figure 5 some Residence Time Distributions (RTD) obtained for the HR3 configuration are shown, with the measured tracer concentration profiles at the reactor’s inlet

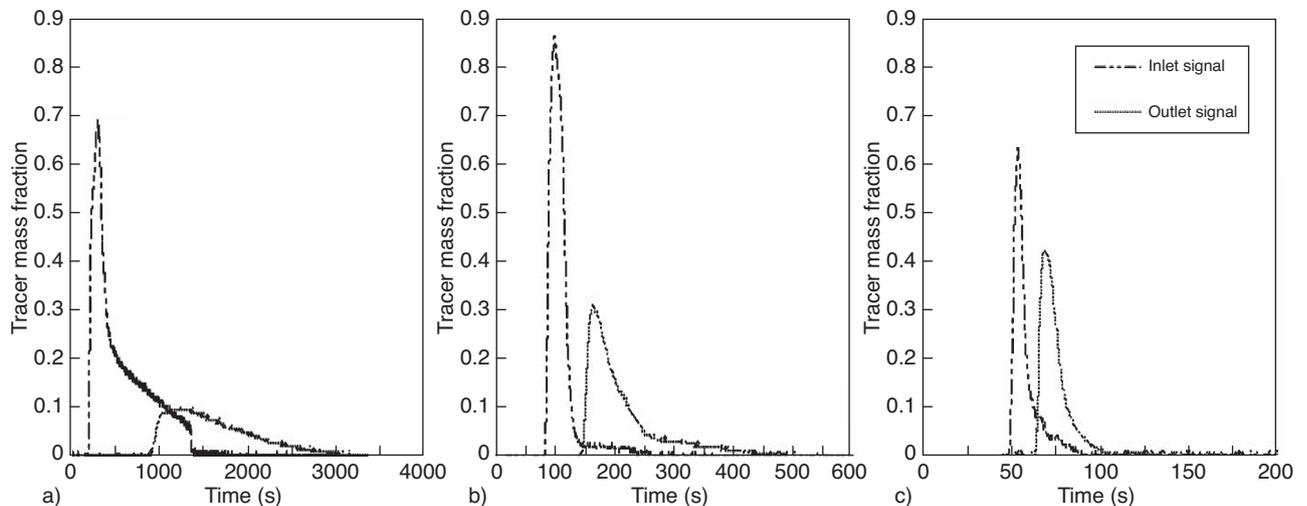


Figure 5
Residence time distributions (inlet and outlet signals) in HR3 configuration for different liquid flow rates: a) 0.1 L/h; b) 0.7 L/h; c) 3 L/h.

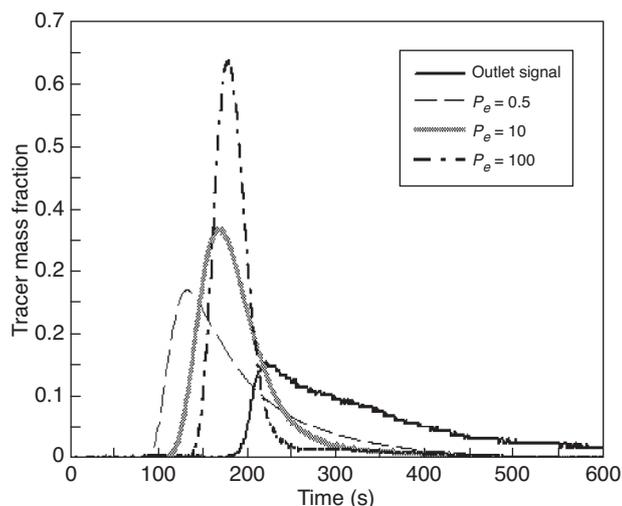


Figure 6

Experimental outlet signal and results of the application of an axial dispersion model to the inlet experimental signal for a liquid flow rate of 0.5 L/h in HR2 configuration.

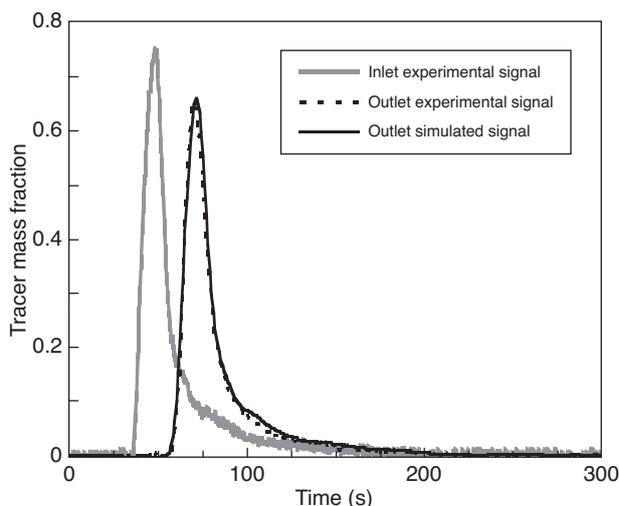


Figure 7

Experimental outlet signal and results of the application of an axial dispersion model to the inlet experimental signal for a liquid flow rate of 1 L/h and a gas flow rate of 10 L/h in HR3 configuration.

1.3.2 Two-Phase Flow Results

The two-phase flow characterization was performed by the analysis of the RTD curves. A more detailed explanation of this analysis is described in Hipolito *et al.* [18]. In all configurations and for every gas and liquid flow rate, the simulated outlet signal represents the experimental results well: the reactor is operated in plug flow regime. An example of the results is presented in Figure 7: the classical axial dispersion model fits the measured data correctly.

Liquid hold-up values (the ratio between the liquid volume and the void volume) were estimated from liquid mean residence time, which was deduced from the RTD model. The measured hold-up values for the HR1 configuration are presented in Figure 8 as a function of the u_{Gs}/u_{Ls} ratio. The liquid hold-up results concerning the HR2 and HR3 configurations have a similar trend to those in Figure 8 and are presented in Hipolito *et al.* [18].

The liquid hold-up exhibits high values (>0.6) in all flow rate conditions. This, and the flow visual observations, indicate that the catalyst should always be wetted, even at the highest u_{Gs}/u_{Ls} ratios. This hypothesis was confirmed by a qualitative study of wetting, in which a dye was injected into the channel filled with porous alumina beads: all beads ended up completely red in a few seconds.

The liquid hold-up decreases from 1 (no gas) to an asymptotic level as the u_{Gs}/u_{Ls} ratio increases. Kallinikos and Papayannakos [17] had already observed a similar trend in circular channels. These results are in agreement with the visual observations of the flow regimes. At high u_{Gs}/u_{Ls} ratios

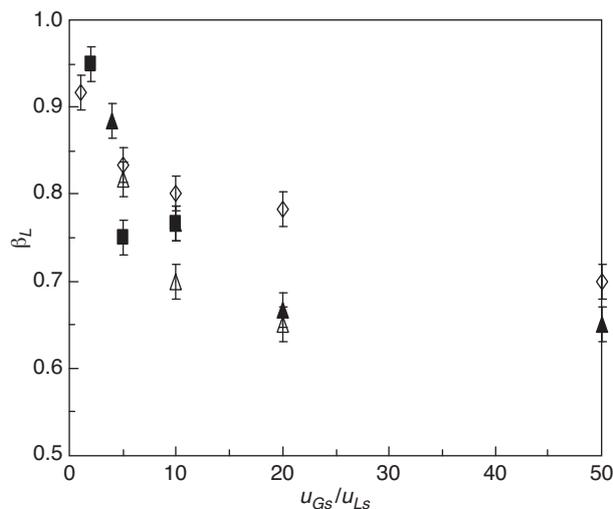


Figure 8

Liquid hold-up as function of the u_{Gs}/u_{Ls} ratio, in HR1, for different liquid flow rates: 0.02 L/h (\diamond), 0.1 L/h (\diamond), 0.5 L/h (\triangle), 1 L/h (\triangle) and 3 L/h (\blacksquare).

(≥ 10), long gas bubbles were observed in the upper part of the channel (low values of liquid hold-up). In these conditions, the flow pattern is “stratified” and so, when the gas flow rate increases, the slip velocity between the gas and liquid phases increases without modifying the liquid hold-up. The liquid flow remains trapped by the solid pellets’ structure. This asymptotic value is independent of the liquid flow rate and the d_p/D_R ratio has a small impact on it. Its value is

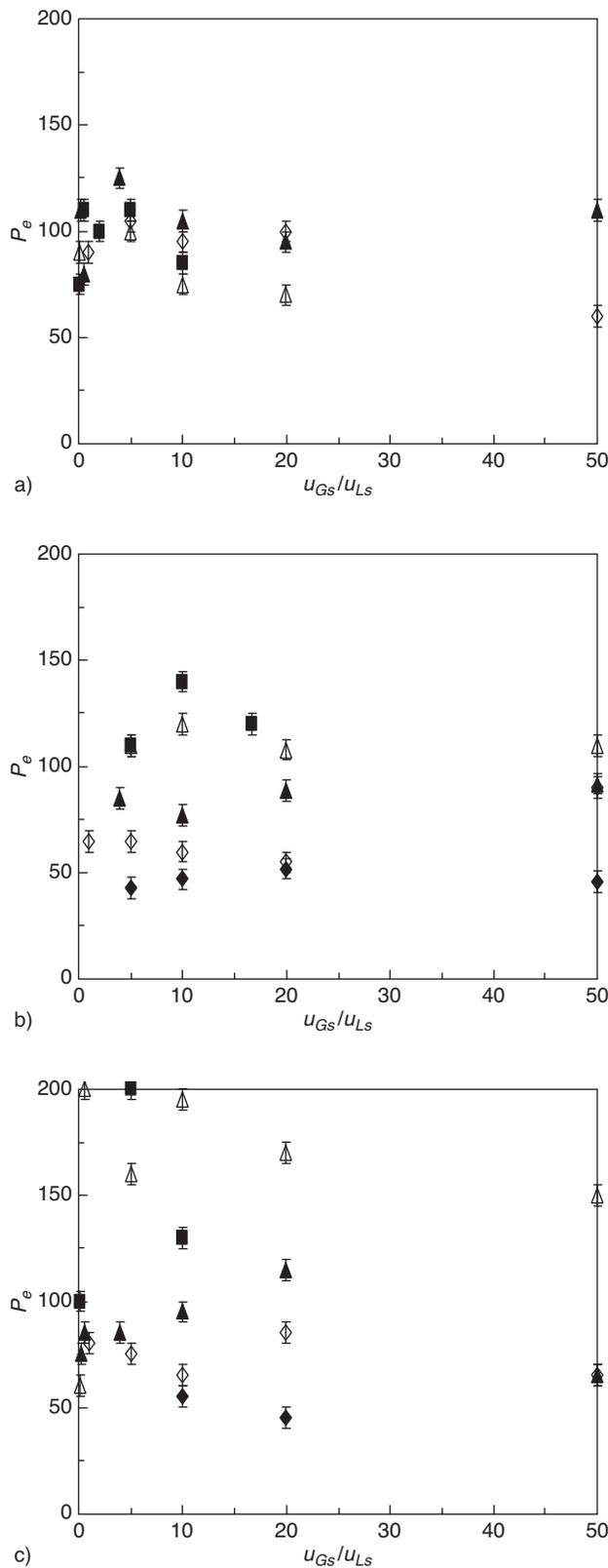


Figure 9
 Peclet number as a function of the u_{Gs}/u_{Ls} ratio, in HR1 a), HR2 b) and HR3 c), for different liquid flow rates: 0.02 L/h (■), 0.1 L/h (◇), 0.5 L/h (▲), 1 L/h (△) and 3 L/h (●).

around 0.65 in the HR1 and HR3 configurations and 0.75 in HR2.

For small u_{Gs}/u_{Ls} ratios, small isolated gas bubbles flow in the channel, and the liquid hold-up remains high. For a constant liquid flow rate, when the u_{Gs}/u_{Ls} ratio increases, the gas bubble length increases and consequently, the liquid hold-up decreases until it reaches the “stratified” regime where the liquid hold-up becomes constant.

The Peclet numbers obtained from the application of the axial dispersion model are presented in Figure 9 for the three configurations tested.

All the Peclet numbers are higher than 40. This result indicates that in the two-phase flow configuration, the reactor behavior is close to that of an ideal plug flow reactor, independently of the flow regime. Compared with the single-phase liquid results, it appears that adding a gas phase makes the flow closer to plug flow. As liquid hold-up decreases, the liquid velocity is increased, and we propose that the detrimental effect of the molecular radial diffusion on the axial dispersion vanishes.

1.4 Pressure Drop

1.4.1 Single Liquid Phase Flow

In Figure 10, the single liquid phase flow pressure drop results are shown, in the three configurations tested.

As expected, the single liquid phase flow pressure drop increases with the liquid flow rate, due to an increase in the friction between the liquid and the solid pellet surface. The pressure drop also increases with the liquid/solid contact surface from 2685 m^2/m^3 for HR2, to 3679 m^2/m^3 for HR3 and

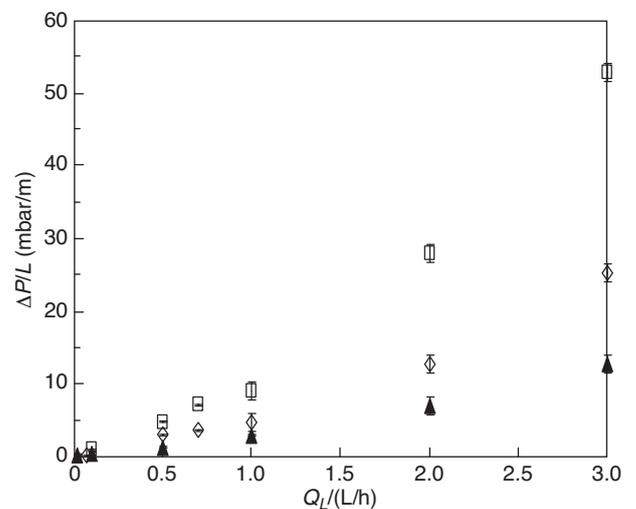


Figure 10
 Single liquid phase flow pressure drop as a function of the liquid flow rate (Q_L) in HR1 (□), HR2 (▲) and HR3 (◇).

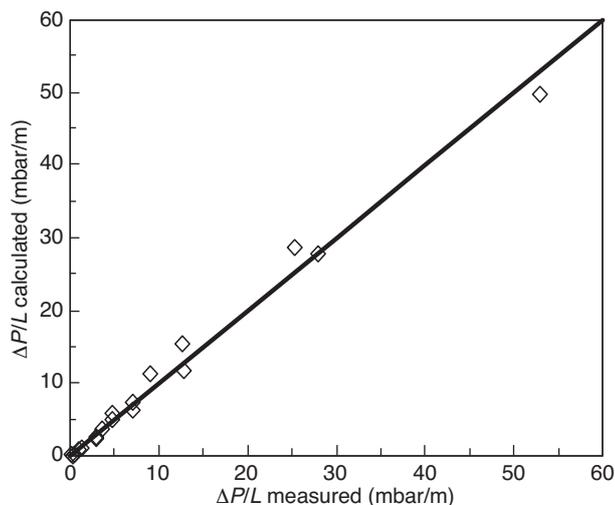


Figure 11

Comparison of measured and calculated (Eq. 1) single liquid phase flow pressure drop per reactor length.

5315 m²/m³ for the HR1 configuration. To interpret the single liquid phase pressure drop results, a modified Ergun equation (Eq. 1) was applied to all the experimental data. In this equation, an equivalent diameter, d_e , was used to take into account the total wetted surface area (Eq. 2) [15].

$$\frac{\Delta P}{L} = E_1 \cdot \frac{\mu_L \cdot u_L \cdot (1-\epsilon)^2}{d_e^2 \cdot \epsilon^3} + E_2 \cdot \frac{\rho_L \cdot u_{Ls}^2 \cdot (1-\epsilon)}{d_e \cdot \epsilon^3} \quad (1)$$

$$d_e = \frac{6 \cdot (\text{Total Volume of Spheres})}{\text{Total Surface Area of Spheres and Wall}} \quad (2)$$

The values for the constants E_1 and E_2 were optimized in order to minimize the sum of the square differences between the experimental and calculated values. The best fit was found for $E_1 = 78$ and $E_2 = 0.34$. These values are somewhat lower than for a standard fixed reactor, as expected, due to lower flow tortuosity (especially near the walls).

As can be seen in Figure 11, the modified Ergun equation represents the experimental data well for the single liquid phase flow pressure drop in all the configurations studied in the single pellet string reactor.

1.4.2 Two-Phase Flow

In Figure 12, the two-phase flow pressure drop results obtained for the HR1, HR2 and HR3 configurations are presented as a function of the u_{Gs}/u_{Ls} ratio.

Similarly to single liquid phase flow, the two-phase flow pressure drop exhibits the highest values in the HR1 configuration and the lowest values in the HR2 configuration. This

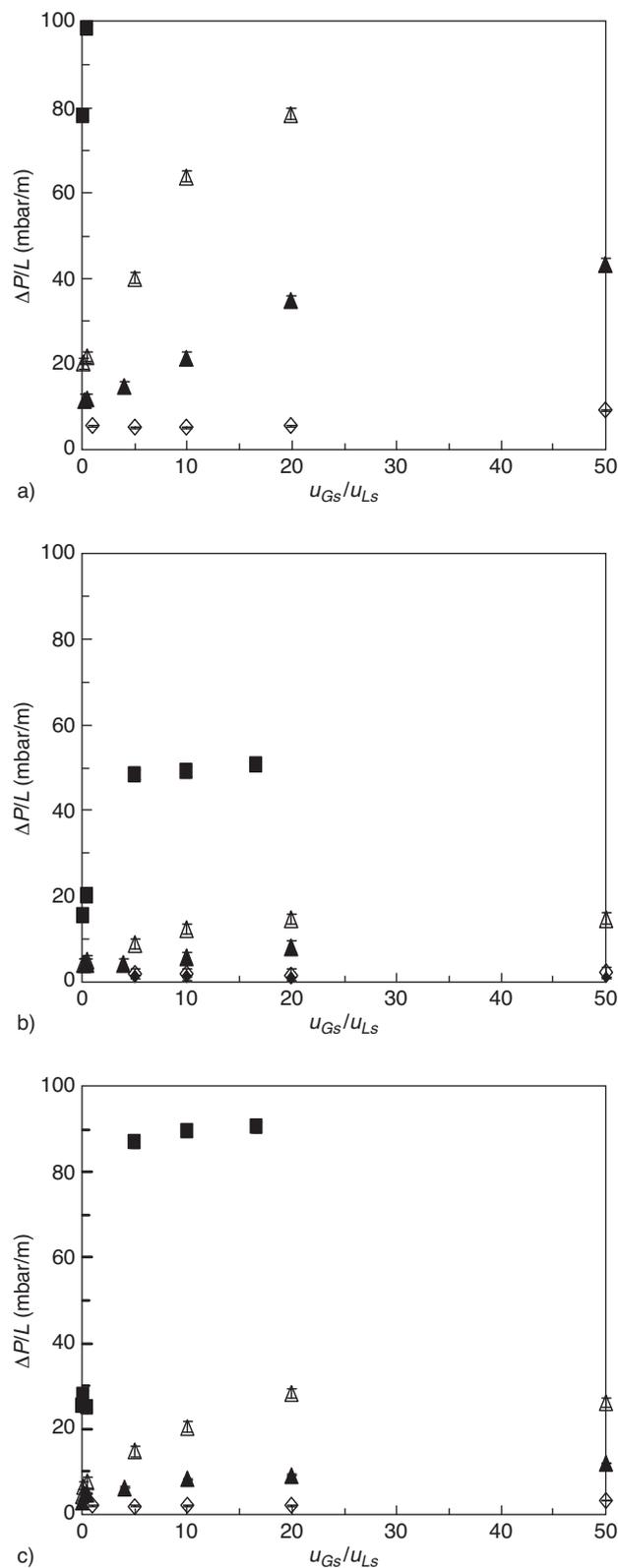


Figure 12

Pressure drop per reactor length as a function of the u_{Gs}/u_{Ls} ratio, in HR1 a), HR2 b) and HR3 c), for different liquid flow rates: 0.02 L/h (\blacklozenge), 0.1 L/h (\diamond), 0.5 L/h (\blacktriangle), 1 L/h (\triangle) and 3 L/h (\blacksquare).

indicates that in two-phase flow, the pressure drop is also controlled by the liquid/solid friction.

In Figure 12, it is possible to distinguish two different zones in all configurations and for all liquid flow rates: a zone, at low u_{G_s}/u_{L_s} ratios, where the pressure drop increases when the gas flow rate increases and another zone, at high u_{G_s}/u_{L_s} ratios, where the pressure drop reaches a constant value. These two zones correspond to the two different flow patterns identified. At low u_{G_s}/u_{L_s} ratios, we are in the “isolated bubbles” regime and so, at a constant liquid flow rate, when the gas flow rate increases, the bubble length increases, which induces a higher friction between the gas and the liquid phases and so, the pressure drop increases. At high u_{G_s}/u_{L_s} ratios, the flow regime is “stratified”. In this regime, the velocity slip between the two phases increases when the gas flow rate increases with almost no influence on overall pressure drop. From these results, it is possible to conclude that gas/liquid friction has a very limited impact on the pressure drop. The u_{G_s}/u_{L_s} ratio that corresponds to the regime transition depends on the liquid flow rate but has a very small dependence on the d_p/D_R ratio.

To predict the two-phase flow pressure drop values in a single pellet string reactor, we plan to test empirical and physical approaches.

2 FIRST RESULTS IN CATALYTIC REACTION CONDITIONS

The string pellet reactor was implemented to perform catalytic tests with a fast hydrogenation reaction. The reactor is composed of six successive modules that are plate reactors. Each module includes a squared channel of $4 \times 4 \text{ mm}^2$ and 1.5 m long machined in a stainless steel plate. The catalyst particles are inserted in the channel. This plate is inserted between two plates machined on the other side to form channels in which a thermal fluid circulates. Thermal control of the fluid allows for an isothermal operation of the reaction zone by both heating up the reactor and removing the reaction heat. The outside view of a module is shown in Figure 13a and a view of the catalytic plate loaded with the catalyst is shown in Figure 13b. The temperature is measured inside the catalytic channel at each module inlet and outlet. Intermediate sampling of liquid and/or by-passing all remaining modules can be after modules number 1, 2 and 4, giving access to both gas and liquid composition after modules 1, 2, 4 and 6 (whole reactor). Liquid and gas phase composition is determined using a gas chromatography analyzer.

To evaluate the potential of this new reactor geometry for catalytic fast reaction tests, the hydrogenation reaction of allene was studied using a spherical-shaped commercial catalyst in all six reactor modules. The liquid feed was composed of 3% in mass of allene and 97% of propene. The feed flow rate was adjusted in order to have a LHSV between 67 and

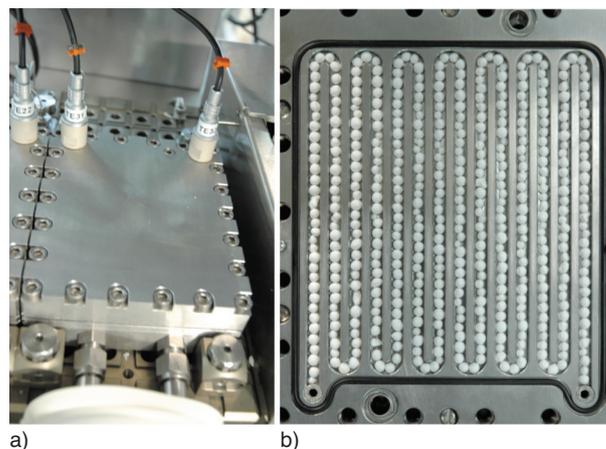


Figure 13

Plate reactor used for catalytic reaction tests: a) top view of a plate reactor module, b) intermediate plate with loaded catalyst bed.

200 h^{-1} . The LHSV is defined as the ratio between liquid feed flow rate over the total catalytic bed volume. This corresponds to a range from 1 to 3 in flow velocities inside the catalytic channel. The hydrogen flow rate was controlled so that the H_2 to allene molar ratio was from 0.5 to 1.5.

The conversion of allene was measured along the catalytic bed length by measuring the composition of the whole flow at the reactor outlet and by progressively by-passing the modules starting from the end. The conversion is plotted in Figure 14 as a function of module number for the lower liquid flow rate corresponding to a LHSV of 67 h^{-1} (based on the whole catalytic volume) and for 3 different ratios of hydrogen to allene molar ratio. It can be seen that conversion increases from the first to the 4th modules to reach a steady value between the 4th and the 6th modules: all the hydrogen is converted after the 4th module, there is an excess in catalyst volume. This hydrogenation reaction is very fast: to measure catalyst activity, it is necessary to operate with LHSV higher than 100 h^{-1} .

In a conventional pilot reactor, LHSV values larger than 100 h^{-1} cannot be reached due to constraints on the maximal feed flow rates (equipment and pressure drop) or the minimal catalytic volume to be loaded (bed length becomes too short). A usual trick is to dilute the catalyst; however, a high dilution level cannot be used in a standard pilot unit as it becomes very difficult to have catalyst particles homogeneously distributed inside the bed and to make sure they all are in contact with a similar amount of gas and liquids of the same composition. With a single pellet string reactor, catalyst dilution is not a problem as all catalytic grains are exposed to the whole liquid and gas flow with the same gas to liquid ratio. Catalyst dilution can be done either by alternating inert and catalytic grains or by inserting catalytic grains only in one

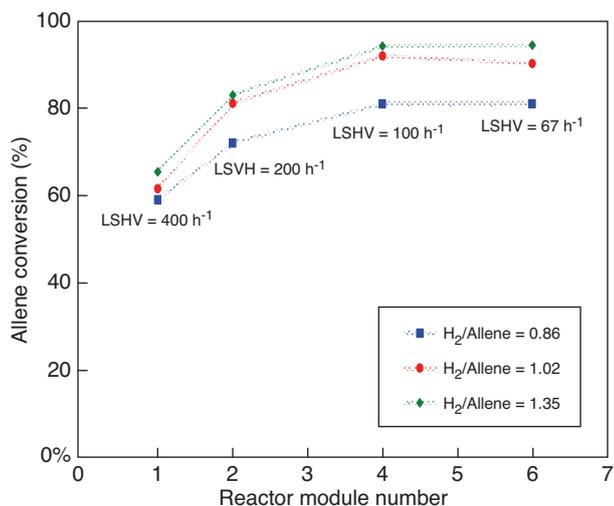


Figure 14

Allene conversion as a function of catalytic bed length: LHSV indicated on the graph are based on the amount of catalyst effectively seen by the feedstock at this point of the reactor.

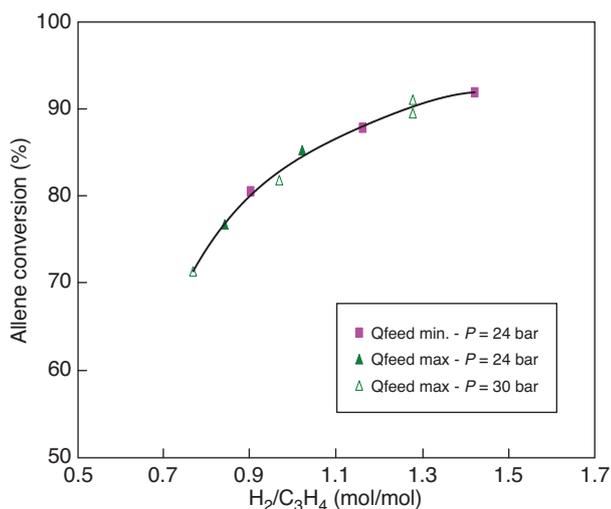


Figure 15

Allene conversion measured on the single pellet string reactor as a function of H₂ over C₃H₄ molar ratio for different liquid velocities and pressures inside the reactor.

part of the channel, the rest being filled with inert particles. We expect to be able to run tests at LHSV of 1200 h⁻¹ with this dilution protocol. The ability to reach very high LHSV on a single pellet string reactor, for example by catalytic bed dilution, is a very interesting feature for fast catalytic reaction study.

As discussed earlier, when using a pilot reactor, it is crucial to know whether it operates in the kinetic regime and whether a model is required to interpret the experimental

data. A standard procedure is to run tests at identical LHSV but with varying flow rates, which is equivalent to varying the catalyst amount. Mass transfer coefficients, both liquid to solid and gas to liquid, increase with feed flow rate, so that, in the kinetic regime, a variation in the feed flow rate should have no effect on conversion. In Figure 15, the results obtained by varying the feed flow rate by a factor of 3 are presented in filled symbols (square and triangle). Conversions are in the same trend, hinting that this hydrogenation reaction is not limited by hydrogen mass transfer in the string pellet reactor. A further confirmation of the absence of hydrogen transfer limitation is the result in the empty triangle in Figure 15. A pressure change should have an impact on the hydrogen concentration at equilibrium (driving force), on the interfacial area and on the mass transfer coefficients when changing gas/liquid flow patterns. However, we observe that conversion is in the same trend for 24 and 30 bar. This hints again that the reaction is slower than the mass transfer external to catalytic grains. We conclude that it is possible to get kinetics data with this new pilot plant reactor for fast reaction.

CONCLUSIONS

A new intensified pilot plant reactor is proposed to test new catalysts for fast reaction processes: a single pellet string reactor. This reactor should help to access real kinetic performances of catalysts without implementing a large amount of catalyst and feed during process scale-up studies.

A hydrodynamic study of liquid and gas/liquid flow in this new kind of reactor geometry was carried out in a horizontal 4 × 4 mm² square section channel filled with spherical particles of 2.0, 3.0 and 4.0 mm diameter. Two main regimes were identified: the “isolated bubbles” regime (at low u_{Gs}/u_{Ls} ratios) and the “stratified” regime (at high u_{Gs}/u_{Ls} ratios) from visual observations and from the analysis of the pressure drop and liquid hold-up data.

The RTD analysis showed that the flow is not plug flow in single liquid phase flow. However, when a gas phase is added, the hydrodynamic becomes close to plug flow configuration (Peclet numbers always higher than 40). The measured values of liquid hold-up are higher than 0.6, for all gas/liquid flow rate conditions. Complete wetting was confirmed by colorimetric tests.

The pressure drop was measured in liquid and gas/liquid flows and appeared to be controlled by the liquid/solid friction surface. For identical superficial velocities, the pressure drop values in the single pellet string reactor studied are between 1 and 20 mbar/m compared with values between 20 and 50 mbar/m in a standard fixed bed pilot reactor. Therefore, even with higher bed length, the pressure drop in a single pellet string reactor remains moderate and allows tests in quasi-iso-pressure conditions.

In general, from a hydrodynamic point of view, the single pellet string reactor appears to be well suited for catalytic tests in gas/liquid reaction conditions.

The first reaction data acquired with a commercial catalyst for hydrogenation of allene are presented. It has been shown that it was possible to get a profile of allene conversion along the bed length with very high LHSV values. The reactor allows one to reach high LHSV with standard flow rates thanks to a high catalyst dilution ratio. Such high LHSV are needed to get kinetics parameters for very fast catalytic reaction. Finally, it has been shown that allene measured conversions do not vary with feed flow rate and pressure change: this indicates that there is no external mass transfer resistance even for such fast reaction conditions.

ACKNOWLEDGMENTS

This study was performed with funding from the Lyon & Rhône-Alpes Chemicals/Environment International Competitiveness Cluster (AXELERA).

REFERENCES

- Gierman H. (1988) Design of Laboratory Hydrotreating Reactors: Scaling Down of Trickle-flow Reactors, *Appl. Catal.* **43**, 277-286.
- Mears D.E. (1971) The role of axial dispersion in trickle flow laboratory reactors, *Chem. Eng. Sci.* **26**, 1361-1366.
- Giese M., Rottschäfer K., Vortmeyer D. (1998) Measured and modelled superficial flow profiles in packed beds with liquid flow, *AIChE J.* **44**, 484-490.
- Berger R.J., Pérez-Ramirez J., Kapteijn F., Moulijn J.A. (2002) Catalyst Performance Testing: the Influence of Catalyst Bed Dilution on the Conversion Observed, *Chem. Eng. Sci.* **90**, 173-183.
- Sie S.T. (1996) Advantages, Possibilities, and Limitations of Small scale testing of catalysts for fixed bed processes, *Revue de l'Institut Français du Pétrole* **46**, 4, 501-515.
- Herskowitz M., Carbonell R.G., Smith J.M. (1979) Effectiveness Factors and Mass Transfer in Trickle-Bed Reactors, *AIChE J.* **25**, 2, 272-283.
- Khadilkar M.R., Wu Y., Al-Dahhan M.H., Dudukovic M.P., Colakyan M. (1996) Comparison of Trickle-Bed and Upflow Reactor Performance at High Pressure: Model Predictions and Experimental Observations, *Chem. Eng. Sci.* **51**, 10, 2139-2148.
- Meille V., Pestre N., Fongarland P., de Bellefon C. (2004) Gas/Liquid Mass Transfer in Small Laboratory Batch Reactors: Comparison of Methods, *Ind. Eng. Chem. Res.* **43**, 924-927.
- Guo J., Shah D.B., Talu O. (2007) Determination of Effective Diffusivities in Commercial Single Pellets: Effect of Water Loading, *Ind. Eng. Chem. Res.* **46**, 2, 600-607.
- Li T., Xu M., Zhu B., Fang D. (2002) Intraparticle diffusion efficiency factor of irregular A301 ammonia synthesis catalyst, *J. Chem. Ind. Eng.* **53**, 12, 1260-1264.
- Scott D.S., Lee W., Papa J. (1974) The measurement of transport coefficients in gas-solid heterogeneous reactions, *Chem. Eng. Sci.* **29**, 11, 2155-2167.
- Sharma R.K., Cresswell D.L., Newson E.J. (1991) Effective diffusion coefficients and tortuosity factors for commercial catalysts, *Ind. Eng. Chem. Res.* **30**, 7, 1428-1433.
- Tottrup P.B. (1982) Evaluation of Intrinsic Steam Reforming Kinetic Parameters from Rate Measurements on Full Particle Size, *Appl. Catal.* **4**, 377-389.
- Li J., Pan Y., Chen M., Zhu B. (1995) Reaction Kinetics for Olefin Hydrogenation over Cobalt-molybdenum Hydrotreating Catalyst and Model Study of Catalyst Properties, *Fuel Sci. Technol. Int.* **13**, 7, 857-879.
- Lee M., Shen S., Chung T., Kuei C. (1984) Flow and Dispersive Behaviors of Cylindrical Pellet String Reactor, *AIChE J.* **30**, 4, 639-641.
- Kallinikos L.E., Papayannakos N.G. (2007) Operation of a Miniscale String Bed Reactor in Spiral Form at Hydrotreatment Conditions, *Ind. Eng. Chem. Res.* **46**, 5531-5535.
- Kallinikos L.E., Papayannakos N.G. (2007) Fluid Dynamic Characteristics of a Structured Bed Spiral Mini-Reactor, *Chem. Eng. Sci.* **62**, 5979-5988.
- Hipolito A., Rolland M., Boyer C., de Bellefon C. (2009) Single pellet string reactor two-phase flow hydrodynamics: results on a square-channel with spherical particles, *GPE-EPIC*, Venice (Italy), 2009.

Final manuscript received in September 2009
Published online in September 2010

Copyright © 2010 IFP Energies nouvelles

Permission to make digital or hard copies of part or all of this work for personal or classroom use is granted without fee provided that copies are not made or distributed for profit or commercial advantage and that copies bear this notice and the full citation on the first page. Copyrights for components of this work owned by others than IFP Energies nouvelles must be honored. Abstracting with credit is permitted. To copy otherwise, to republish, to post on servers, or to redistribute to lists, requires prior specific permission and/or a fee: Request permission from Documentation, IFP Energies nouvelles, fax. +33 1 47 52 70 78, or revueogst@ifpenergiesnouvelles.fr.