Science@ifpen
Issue 18 - October 2014

The fundamental changes in progress, in today's world energy landscape, are driving the need for innovation through the development of new process, catalysts and formulations. To step up these developments, we need to overcome some major scientific hurdles related to the identification of descriptors for the design, to the modeling of closely coupled phenomena and to the characterization of materials and fluids for energy. It is against this background that IFPEN's researchers are working on:

- ***reactivity-structure-composition relationships** in oil feeds and biomass;*
- ***multiscale, multiphysical modeling approaches;***
- ***control of phenomena** present in development tools;*
- ***experimental equipment** and **methodologies.***

These developments are helping to reinforce our industrial property and scientific visibility, with the annual publication of around 70 patents and 30 articles in high-impact journals.

We hope that you enjoy this issue.

Luc Nougier, Director
Process, Design and Modeling Division
Dominique Humeau, Director
Process Experimentation Division

Pilot unit reactors: *alea cata est!*

IFPEN is carrying out research to improve or develop catalysts for refining and petrochemical processes. A large proportion of the performance assessments on new catalysts is carried out in fixed-bed reactors, in which the catalyst grains are randomly packed. This raises the question of the influence of these random effects on the reaction performance of a test reactor and on the representativity of the operating conditions with respect to real processes.

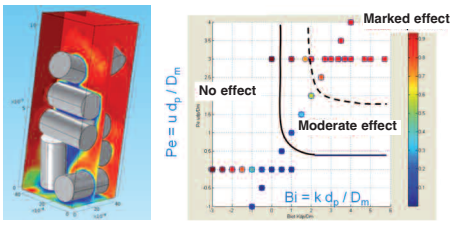
This effect could have an even greater impact given that the tests are conducted in increasingly small reactors, for reasons related to both the limited volume of the material to be tested and operating costs. Furthermore, for reasons related to hydrodynamics, size reductions are achieved more by adjusting the diameter of the reactor rather than its length, further exacerbating the non-repeatable nature of the stacking layers, particularly the void fraction, and their potential consequences on reactions.

It was therefore necessary to gain a better understanding of these random effects of stacking on the reliability and representativity of the results and, conversely, on the design criteria leading to a repeatable reactor performance.

Partial responses are supplied by numerical flow simulations coupled with mass transport and reactions in random or structured packed beds. Calculations were performed on a scenario with eight cylindrically-shaped model grains. The results indicate that the performance of the reactor, in terms of material transfer or chemical conversion, are highly dependent on the arrangement of the grains when molecular diffusion is not fast enough to ensure uniformity of the concentration gradients induced by the reaction and by the flow. This tends to prove a shared origin between the sensitivity to stacking and the physics governing the limitation to external mass transfer.

This research is being continued within the context of two theses, examining respectively:

- the characterization of the stacked layers and the influence of their structure on single phase flows, for spherical and cylindrical grains;
- and the intrinsic effects of the shape of the catalyst grains (trilobe, quadrilobe), on the void fraction, flows and reactions in packed beds.



Left: Concentration range in an eight-cylinder bed. Right: first map of random effects.

M. Rolland, "Des limites à la réduction d'échelle en réacteur de test catalytique en lit fixe ?", *thesis defended on 7/7/2014, Claude Bernard Lyon 1 University.*

Scientific contact:
matthieu.rolland@ifpen.fr

Stirred, not shaken!

Blending and reaction in stirred tanks are frequent operations in several industries. These devices' operation can involve a multitude of complex and simultaneous phenomena, as well as both homogeneous and heterogeneous reactions.

Achieving the desired degree of blending or dispersion, or reaction yield, while reducing side-reactions, requires the appropriate setting of operating conditions and mechanical design parameters.

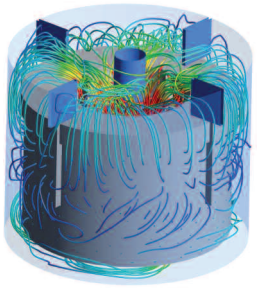
Since the flow in stirred reactors can depend on numerous interacting phenomena, their simulation using Computational Fluid Dynamics (CFD) tools can prove to be a quite challenging task.

At IFPEN, CFD has been used for the simulation of stirred reactors, both at the pilot and industrial plant scales. It has been providing a better understanding of their way of operation that can lead to changes in design choices or in operating conditions, resulting in the intensification of process.

One example of experimentation intensification concerns stirred tank reactors for kinetic testing of commercial catalysts in liquid or two-phase gas/liquid media. This equipment produces a highly complex turbulent and multiphase flow. However, it is essential to ensure that mixing or mass transfer are not affecting the value determined for the reaction rate, especially for fast reactions. CFD is being used to simulate the flow under different conditions, what allows defining regimes of kinetic control, on which the true reaction rate can be measured.

Generally speaking, the use of computational modeling significantly reduces the need for experimentation. This approach also offers an important alternative to empirical design rules, with undeniable benefits in terms of project development time and cost.

Scientific contacts:
vania.santos@ifpen.fr
claudio.fonte@ifpen.fr



Flow streamlines obtained from CFD in a stirred tank reactor with a stationary catalytic basket.

C.P. Fonte, B.S. Pinho, V. Santos-Moreau, J.C.B. Lopes. Prediction of the Induced Gas Flow Rate from a Self-Inducing Impeller with CFD. *Chemical Engineering & Technology, 2014, 37 (4), 571–79. DOI:10.1002/ceat.201300412*

V. Santos-Moreau, L. Brunet-Errard, M. Rolland, Numerical CFD simulation of a batch stirred tank reactor with stationary catalytic basket. *Chemical Engineering Journal, 2012, 207-208, 596-606. DOI:10.1016/j.cej.2012.07.020*

Recovering well when things get hot

Reducing the impact of its activities on the environment is a priority for the chemicals industry. Recovering heat produced by processes, using heat exchanger networks, is one of the strategies to achieve this.

Pinch* analysis is currently the best known method for analyzing and optimizing these heat exchanger networks (HENs). However, its main limitation is that it does not incorporate the feasibility criteria engineers need to deal with in practice. Furthermore, the heuristic rules that it uses become very difficult to apply when the case considered includes a substantial number of flows.

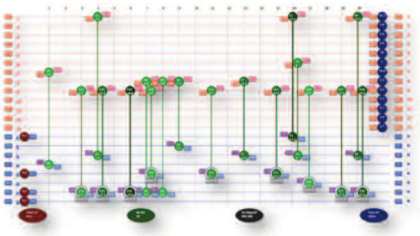
IFPEN's researchers have developed a computer modeling and optimization tool of HENs. This makes it possible, for example, to take into account constraints related to the use of real "2 pass/1 pass" heat exchangers, impossible to deal with directly using the Pinch method. It also makes it possible to avoid configurations that are problematic in terms of safety.

This tool uses hundreds of linear equations, solved using a Mixed Integer Linear (MILP) solver in order to optimize an "objective function". This links technical data to an economic value via a simple linear approximation. The method is iterative and progressively integrates additional constraints, taking into account the feasibility of the solutions proposed by the solver.

This new approach enables better incorporation of operator flexibility in the design of HENs. The latter are thus optimized in both energy and technological terms, with, in addition, the provision of information on investment and operating costs (CAPEX and OPEX). The energy consumption calculated can then be compared with the optimum resulting from the Pinch analysis, making it possible to identify levers for improvement.

In addition, the methodology developed is also effective for analyzing industrial processes with a view to revamping them.

The use of a more elaborate solver (non linear – MILP) should make it possible to avoid a number of restrictive hypotheses and to extend the application scope of the method, by improving the model structure, the extent of handled constraints and the "objective function".



Example of the calculation result concerning a heat exchanger network generated from 21 flows and data processes.

* Method used to determine a theoretical energy optimum complying with thermodynamic principles and using heuristic rules to determine a HEN.

T. Plennevaux , R. Digne, H. Dreux, F. Feugnet, Utilisation industrielle d'une méthode numérique d'optimisation d'un réseau d'échangeurs. *Récents Progrès en Génie des Procédés, 104 – 201*

Scientific contact:
thomas.plennevaux@ifpen.fr

Industrial fixed-bed catalytic reactors: starting out from the nano scale

The fixed-bed catalytic procedures designed by IFPEN are used in a large number of oil cut hydrotreatment processes. A capacity to anticipate their performance is therefore a competitive advantage when it comes to accurately determining the dimensions of equipment and reducing their costs (CAPEX). To do this, it is necessary to know how to conduct coupled modeling of the various phenomena involved — both physical and chemical — on various scales, from the active site to the catalytic bed.

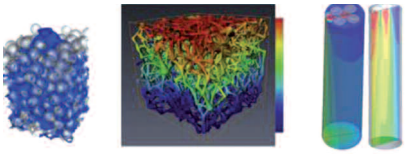
The strategy adopted is based on local modeling approaches, followed by integration on larger scales, right up to the reactor scale. The overall model can then be used both for innovative design (for example as part of a process intensification approach) and for preventive analysis relating to the consequence of a malfunction.

On a catalyst active site scale, micro-kinetic models are developed in order to integrate competitive adsorption phenomena between species and the elementary chemical reactions that occur. By taking into account highly complex reaction networks, the micro-kinetic approach then makes it possible to determine one or more macroscopic models summing up the most probable reaction paths. The initial kinetic parameters are then determined using molecular modeling calculations.

On a catalyst grain scale, modeling of surrounding flows enables estimation of the wetting rate, followed by determination of its impact on the catalyst's reaction efficiency, using 2D grain models.

On a catalytic bed scale, models based on pore networks and CFD calculations, using a Volume of Fluid approach, make it possible to predict the distribution of flows in the bed (cf. Figure). These models are fed by experimental data obtained from reactors with variable diameters (1 to 60 cm), using advanced instrumentation methods such as MRI, γ-ray tomography, and optical sensors.

On a global reactor scale, a methodology to study the thermal stability of reactors has also been developed. This method enables the construction of stability maps and the adjustment of both dimensions and operating conditions to ensure the risk-free operation of industrial catalytic reactors.



Flow modeling in an unstructured fixed bed.

F. Augier, *A. Koudil,* ***A. Royon-Lebeaud,*** *L. Muszynski, Q. Yanouri,* Numerical approach to predict wetting and catalyst efficiencies inside trickle bed reactors. *Chem. Eng. Science, 2010, 65, 1, 255-260.*

J.-M. Schweitzer, ***C. Lopez Garcia, D. Ferre,*** Thermal runaway analysis of a three-phase reactor for LCO hydrotreatment. *Chem. Eng. Science, 2010, 65, 1, 313-321.*

Scientific contact:
jean-marc.schweitzer@ifpen.fr

Multi-scale simulation for gas cleaning cost reduction

In its most recent scenarios, the International Energy Agency (IEA) highlights the strong growth in world demand for natural gas to occur from now to 2035 and talks about a "golden age for gas". However, over 40% of conventional natural gas reserves are considered to be sour and will require cleaning of the gas produced in order to meet increasingly severe specifications. Gas sweetening using amines is a widespread gas cleaning process that is based on a gas-liquid counter-current absorption technology.

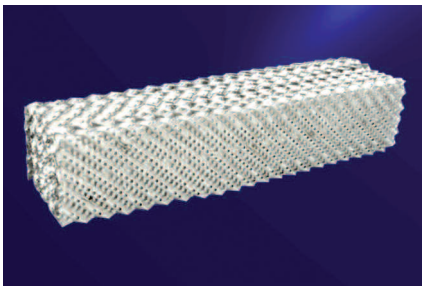
The improvement and development of gas-liquid technologies are among the most significant routes for progress in this field, with the key component being the packing material through which fluids circulate inside the absorption columns (cf. Figure). These packings must compromise between capacity (flow treated) and efficiency (treatment quality), which is synonymous to size reduction, both in diameter and height, of industrial units.

To this end, for specified operating conditions, the performance of a packing is determined on the basis of its geometry, which has a direct impact on pressure drop as well as on the mass transfer rates, via the interfacial area and the mass transfer coefficients.

Today, multi-scale CFD simulation is emerging as a powerful tool for predicting hydrodynamics and transfer rates within packings. This approach is being developed at IFPEN via specific numerical methods, at scales ranging from those of the trickle liquid film to the column, i.e. a scale ratio of 1/106, incorporating the interactions between the packing and the gas or liquid distribution systems inside the column[1].

This approach has driven innovation, contributing to the development of the IFPACC™ 2X packing, a product that offers a highly competitive performance and which is now marketed by Prosernat (September 2014).

IFPEN is continuing the development of its expertise in the field of multi-scale simulations via internal developments and partnerships with renowned academic players [2, 3].



1-m block of IFPACC™ 2X packing for filling industrial absorption columns.

1) ***L. Raynal, A. Gomez, B. Caillat, Y. Haroun,*** *2013. http://dx.doi.org/10.2516/ogst/2012104*

2) ***M. Fourati,*** *V. Roig,* ***L. Raynal,*** *2013. http://dx.doi.org/10.1016/j.ces.2013.02.041*

3) ***Y. Haroun,*** *D. Legendre,* ***L. Raynal,*** *2010. http://dx.doi.org/10.1016/j.ces.2009.07.018*

Scientific contact:
manel.fourati@ifpen.fr

Enzyme cocktail for hydrolysis: a recipe that's far from simple

The production of 2nd-generation bioethanol from lignocellulosic biomass is one of the options being examined to reach European targets for the incorporation of biofuels by 2020. One of the key steps in the process is enzymatic hydrolysis, which consists in converting lignocellulose into fermentable sugars using specific enzyme cocktails derived from industrially-produced fungi, such as *Trichoderma reesei.*

To improve this step and make the process economically viable, IFPEN is employing complementary strategies:

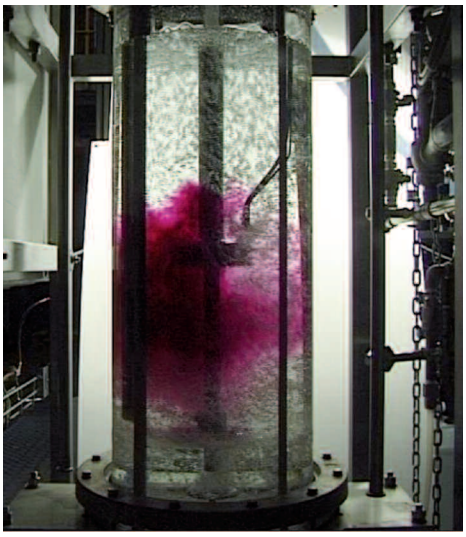
- improve enzyme strains derived from *Trichoderma reesei* in order to produce more powerful cocktails (cf. *Science@ifpen n° 16*);
- optimize bioreactors in order to maximize enzyme production;
- minimize the enzyme doses required for hydrolysis.

Point 2 requires control of local hydrodynamics (mixing, shear, transfers) in the reactor, as well as their effects on the metabolism of the fungi. Experimental studies have been carried out on bioreactors of various sizes in order to examine the effect of changing the scale and medium rheology on oxygen transfer and mixing quality. In particular, a gas-liquid transfer coefficient model integrating the shear-thinning rheology of the medium and the mean shear has been developed and validated on a pilot scale (6 m^3 reactor).

For point 3, the aim is to understand the mechanisms involved in interactions between the various enzyme families and the lignocellulosic substrate. First of all, the experimental part allowed to study the initial kinetics of the different enzymes on a model substrate, Avicel cellulose. Then, over a period of several days, complex substrates, such as delignified straw, were examined. This research led to the development of a predictive model capable of taking into account the composition of the enzyme cocktail, the quality of the substrate to be hydrolyzed and the hydrolysis operating conditions.

The work will be supplemented by the development of new *in situ* analysis methods and continued by a study of the pretreatment step. Substrates that are very different in terms of their morphological characteristics and reactivity will therefore be sought and selected.

Scientific contacts:
damien.hudebine@ifpen.fr
frederic.augier@ifpen.fr



Measurement of mixing time by colorimetry in a 42-L tank.

*J.C. Gabelle, **E. Jourdier** , R. Licht, **F. Ben Chaabane, I. Henaut,** J. Morchain, **F. Augier,*** Impact of rheology on the mass transfer coefficient during the growth phase of Trichoderma reesei in stirred bioreactors. *Chem. Eng. Sci, 2012, 75, 408-417.*

*M. Chauve, **H. Mathis**, D. Huc, **D. Casanave, F. Monot, N. Lopes Ferreira,*** Comparative kinetic analysis of two fungal beta-glucosidases. *Biotechnol. Biofuels, 2010, 3, 1-8.*

Innovation

IFP School launches its first MOOC (Massive Open Online Course), entitled Sustainable Mobility: Technical and Environmental Challenges for the Automotive Sector, *which will be delivered in English from 3 to 30 November. In particular, the course includes a serious game designed to aid learning. Enroll now! http://mooc.sustainable-mobility.ifp-school.com*

Scientific visitor

• **Adrian Cérépi,** *director of research at Ensegid within the Institut polytechnique de Bordeaux, has been hosted by the Geosciences Division since 3 July 2014, where he will carry out research for a period of 20 months. His work concerns the impacts of CO_2 on "carbonaceous reservoirs" in the context of enhanced oil recovery (EOR) by CO_2 injection.*

Publications

• *OGST – Revue d'IFP Energies nouvelles – Issue 3, volume 69 – Special issue dedicated to the Colloids 2012 scientific conference*

• *OGST – Revue d'IFP Energies nouvelles – Issue 4, volume 69 – Digital modeling in geosciences*

http://ogst.ifpenergiesnouvelles.fr/

Upcoming scientific events

• *Workshop on **Unlocking Gas Reserves Using Innovative Processes –** 2-3 December 2014, Maison de la Chimie, Paris - www.ws-unlockgas2014.com*

• *IFP Energies nouvelles' "Rencontres scientifiques" event **– LES for ICE –** 4-5 December 2014, IFPEN Rueil-Malmaison - www.rs-les4ice.com*

Awards

• **Cédric Bara,** *a doctoral student from the Catalysis and Separation Division: prize for best oral paper at the 11th International symposium on Scientific Bases for the Preparation of Heteregeneous Catalysts (July 2014)*

• **Delphine Bresch-Pietri,** *a doctoral student in the Mechatronics, Computer Science and Applied Mathematics Division until 2012:* European Best PhD on Control of Complex and Heterogeneous Systems 2013 *prize for her thesis on "Robust control of variable delay systems. Theoretical contributions and engine applications".*

Managing Editor: Marco De Michelis
Editor-in-chief: Éric Heintzé
Editorial committee: Xavier Longaygue, Laurent Forti, Françoise Brucy
Graphic Design: Esquif
ISSN No. 1957-3537

To get in touch with IFPEN or receive Science@ifpen:
Institutional Relations and Communications Division
Tel.: +33 1 47 52 51 34 - Science@ifpen.fr
1 et 4, avenue de Bois-Préau - 92852 Rueil-Malmaison Cedex - France
Press contact: A.-L. de Marignan - Tel.: +33 1 47 52 62 07 — **Institutional contact:** A. Sanière - Tel.: +33 1 47 52 69 19