Science@ifpen

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SPECIAL ISSUE
Publications by young researchers

A kinetic model for complex systems: to what end?*

Post-doctoral research by Julian Becker

Research and training are the pillars of IFPEN activities. Hosting PhD students is therefore an integral part of its strategy, with substantial resources provided by the Scientific Division for "Training through research".

The contribution of these young researchers – still undergoing training – is essential to drive knowledge forward and thus develop the innovations of the future, both through their thesis work and via the partnerships forged with the academic community.

In return, PhD students at IFPEN benefit from an ideal scientific and technological working environment, offering a continuum between fundamental research and innovation, so perfectly illustrated by Yves Chauvin, winner of the Nobel Prize in Chemistry, who passed away in January 2015.

Their work helps to overcome scientific challenges in the fields of energy, transport and climate, and contributes to the development of novel solutions.

This latest edition of our scientific newsletter presents the work of our PhD and post-doctoral researchers, illustrating the diversity and quality of their contributions to IFPEN's research.

Didier Houssin,
CEO, IFPEN

In the field of chemical processes, kinetic models are used in two different contexts:

- to optimize the amount of target products on an industrial scale;
- to gain a better understanding of certain reactions, by decorrelation of the multiple effects involved.

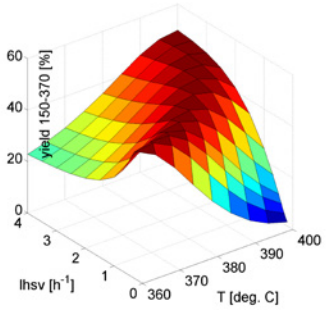
However, the complexity of the active phenomena makes it difficult to develop exhaustive models. The hydrocracking process is a case in point. This process is used to convert crude oils, made up of several thousands of molecules, into gasoline, kerosene and/or diesel. To study it, we rely on either statistical approaches or a detailed description of molecules reactivities.

IFPEN researchers have compared two modeling approaches: firstly, an approach known as Continuous Lumping (CL)[1], which, rather than focusing on individual molecules, looks at model distributions of molecules, with the associated reactivities, which requires a relatively small number of analyses. Secondly, a Single Events (SE) approach, based on a very in-depth description of kinetic mechanisms but requiring highly detailed characterizations that are rarely available in practice.

The two types of models have been shown to be complementary[2]. The CL model leads to precise, rapid simulations, but it cannot perform a fine analysis of the mechanisms involved. The SE model, which is more complicated to implement, deciphers the reaction processes involved more effectively and provides information on the reactivity distributions used in the CL model.

This information is valuable when it comes to proposing innovative solutions relating to catalysts and processes. Investigative research using the SE model is continuing, focusing on specific mechanisms, such as those related to the reactivity of aromatic substances and cyclo-alkanes, as well as on prediction of refined product quality.

*Post-doctoral research entitled **"Modeling of complex reaction systems: from reconstruction of feeds to modeling by consecutive events".**



Determination of maximum kerosene and diesel yield on the basis of hydrocracking process operating conditions (obtained by CL).

(1) *J. Becker, **B. Celse, D. Guillaume, V. Costa,** L. Bertier, **G. Pirngruber, E. Guillon,** Fuel 164, 2016, 73-82.*
DOI: 10.1016/j.fuel.2015.09.057

(2) *J. Becker, N. Serrand, **B. Celse, D. Guillaume,** H. Dulot, Fuel 165, 2016, 306-315.*
DOI: 10.1016/j.fuel.2015.09.091

Scientific contact:
benoit.celse@ifpen.fr

Trapping the bubble...*

Thesis from Élise Alméras

Bubbly flows are involved in several industrial processes, particularly in the field of refining and petrochemicals, and in a variety of reactor configurations (bubble columns, stirred tanks, etc.). Their complex dynamics have not yet been fully characterized, whereas controlling mixing is critical for process optimization.

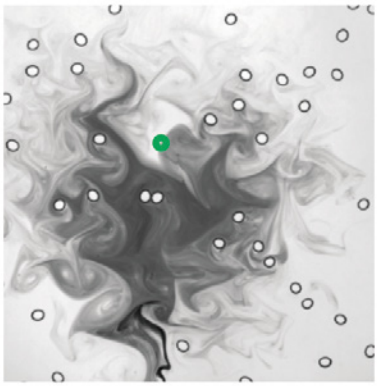
Until now, no model capable of predicting the dispersion of a solute in this type of flow was avalaible. Engineers had no other choice but to develop empirical correlations, expensive in terms of experimentation and presenting risks of errors for the design of large-scale units.

To identify and separate the various mechanisms responsible for mixing, the dispersion of a passive tracer in different experimental elementary configurations was studied. This has resulted in a new physical model to predict the transport of chemical species[1]: based on the physical fluid properties, it predicts the evolution of diffusion coefficients, taking into account the turbulence induced by the bubbles.

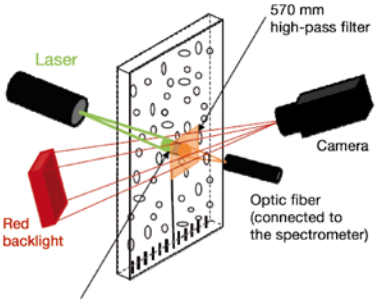
This model was then directly integrated into a CFD[a] simulation tool used at IFPEN. The results obtained by simulation[2] are consistent with those obtained experimentally in complex flows encountered in a cold flow model of several liters.

This research opens up new avenues for the quantitative use of numerical tools to extrapolate and scale-up complex flows for process design.

*Thesis entitled "**Transport and mixing properties in bubbly flows**".



Mixture visualization in a Hele-Shaw cell[b].



Experimental assembly using a Hele-Shaw cell[b].

(1) ***E. Alméras,*** *F. Risso, V. Roig, S. Cazin,* ***C. Plais, F. Augier,*** *Journal of Fluid Mechanics, 2015, 776, 458-474.*
DOI: 10.1017/jfm.2015.338

(2) ***E. Alméras, C. Plais, F. Euzenat,*** *F. Risso, V. Roig,* ***F. Augier,*** *Chemical Engineering Science, 2016, 140, 114-122.*
DOI: 10.1016/j.ces.2015.10.010

a - Computational Fluid Dynamics
b - Quasi-2D configuration, with a thickness of around one millimeter

Scientific contact:
cecile.plais@ifpen.fr

Porous alumina: where is the weakest link?*

Thesis from Déborah Staub

The hydrotreatment process, used to produce fuels meeting environmental specifications, employs alumina-based granular catalysts, the efficiency of which scientists are constantly trying to improve. One way of doing this is to increase their internal porous volume and their specific surface area, but there is a risk involved: that of weakening them mechanically.

And yet the physical integrity of these granules is crucial. Packing them in the reactor can damage them and lead to the formation of "fines" detrimental to the operation of the process. The key parameters controlling the tensile strength of high-porosity aluminas in this configuration must be identified, something that poses a real challenge with samples of such a small size[1]. The approach proposed by IFPEN, in collaboration with Insa in Lyon[a], is based on micromechanical tests combined with small-scale observations and a modeling process.

In the case of catalyst granules, new characterization by indentation has been shown to be useful. The local damage produced by the indenter[b] was studied by scanning electron microscopy (see figure).

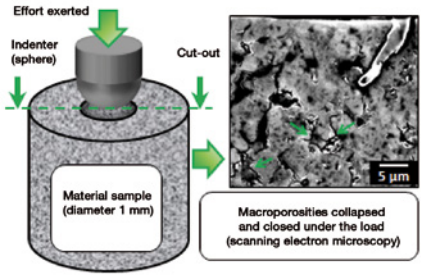
This examination of the microstructure revealed the weak points and identified the mechanism responsible, on this scale, for the macroscopic damage. In this case, the densification observed is the result of collapse of the largest pores (>1 µm).

In addition, for this porous alumina, a rupture criterion inspired by rock mechanics has been identified using an inverse process, based on digital simulation of the test[2].

This research will contribute to the design of catalysts that are optimized both mechanically and from the point of view of their catalytic efficiency.

a - MATEIS Laboratory (MATErials: Engineering and Science)
b - Low diameter, spherical tip

Scientific contact:
vincent.le-corre@ifpen.fr



Schematic diagram of indentation and visualization of damage.

(1) ***D. Staub,*** *S. Meille,* ***V. Le Corre,*** *J. Chevalier,* ***L. Rouleau,*** *OGST 2015, 70, 475-486.*
DOI: 10.2516/ogst/2013214

(2) ***D. Staub,*** *S. Meille,* ***V. Le Corre, L. Rouleau,*** *J. Chevalier,* Identification of a damage criterion of a highly porous alumina ceramic. Submitted to *Acta Materiala.*

*Thesis entitled "**Study of fracture behavior of high-porosity aluminas: application to residue hydrotreatment catalyst supports**".

Supramolecular strategy: the key to selectivity!*

Thesis from Pierre Boulens

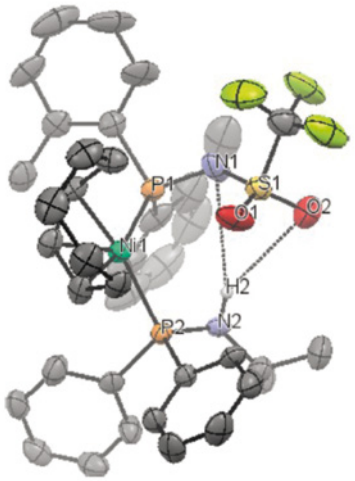
Short-chain alpha-olefins such as butene-1 (C_4), hexene-1 (C_6) or octene-1 (C_8) are major chemical intermediates. Key comonomers in the production of polyethylene, they are primarily obtained from ethylene, *via* catalyzed oligomerization reactions.

However, the main industrial oligomerization processes that exist lead to wide distributions of linear alpha-olefins (C_4-C_{20+}) that do not match market demand, which is more geared towards light olefins (C_4-C_8).

To have more selective processes, an innovative approach for the generation of new nickel-based catalysts has been developed, combining the supramolecular chemistry expertise of the University of Amsterdam and that of IFPEN in the field of homogeneous catalysis. A first phase consisted in focusing on phosphorus ligands, capable of forming supramolecular assemblies *via* hydrogen bonds. It was thus possible to stabilize, isolate and fully characterize a new, highly original family of nickel organometallic zwitterionic[a] complexes, combining sulfonamido-phosphine and amino-phosphine ligands, joined together by hydrogen bonds[1].

These complexes have been shown to be highly active (10 times more than reference catalysts) and robust for the ethylene oligomerization reaction.

In addition, by regulating the nature of the groups brought by phosphorus atoms, it is possible to control the selectivity of the oligomerization reaction, with a view to preferentially producing the butene-1 sought.



Supramolecular nickel-based catalyst characterized by XRD.

The original strategy adopted in this project has led to the emergence of an innovative family of nickel catalysts for ethylene oligomerization, renewing the interest of nickel for this conversion and paving the way for other innovative catalysts. The possibility of adjusting the selectivity of the reaction by regulating the ligands is also a definite advantage in terms of being able to tailor processes to market requirements.

a - Molecules that are neutral overall but present local positive and negative charges

(1) ***P. Boulens, E. Pellier,*** *E. Jeanneau, J.N.H. Reek,* ***H. Olivier-Bourbigou, P.-A. R. Breuil,*** *Organometallics, 2015, 34 (7), 1139-1142. DOI: 10.1021/acs.organomet.5b00*

*Thesis entitled **"Sulphonamido-Phosphorus Nickel Complexes for the Selective Oligomerisation of Olefins".**

Scientific contact:
pierre-alain.breuil@ifpen.fr

Chemoinformatics serving chemical EOR*

Post-doctoral research by Christophe Muller

One of the existing chemical Enhanced Oil Recovery (EOR) methods consists in injecting complex formulations containing surfactants into the reservoir, in order to release the oil trapped by capillary effects. For a given reservoir, choosing an appropriate formulation requires numerous laboratory tests.

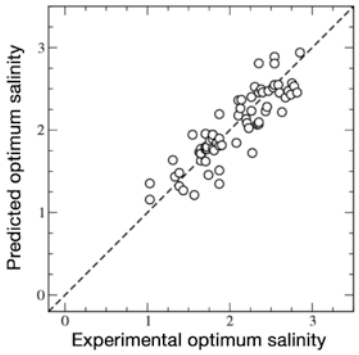
One of the keys for the development of the injected formulation is the control of the optimum salinity, leading to the lowest interfacial tensions in order to maximize the oil recovery. Access to a predictive model for this optimum salinity would speed up the surfactant formulation selection process.

Chemoinformatics – a recent scientific field – provides tools and methods for analyzing and processing chemical data. As long as enough data are available, this approach can identify relevant descriptors and models to predict properties.

A joint project with Solvay, as part of the EOR Alliance, has led to the formation of a database of this type, grouping together, for a temperature, brine and model oil, the optimum salinity experimental values for various surfactant families.

By applying chemoinformatics tools to this database[1], IFPEN researchers have demonstrated that it is possible to directly link the chemical structure of surfactants and the optimum salinity of formulations. The combined use of SVM[a] and functional group counts has led to robust predictive models for these conditions.

The objective now is to develop a model including greater complexity, and then to integrate it into the high throughput selection process for new surfactant formulations.



Comparison between optimum, experimental and predicted salinity values.

a - Support vector machines: Supervised learning methods designed to solve classification and regression problems.

(1) ***C. Muller,*** *A.G. Maldonado, A. Varnek,* ***B. Creton,*** *Energy Fuel, 2015, 29, 4281. DOI: 10.1021/acs.energyfuels.5b00825*

*Post-doctoral research entitled **"Development of an inverse QSPR approach applied to EOR".**

Scientific contact:
benoit.creton@ifpen.fr

Measuring soot in engines: a "sizable" problem*

Thesis from Emre Cenker

Controlling the production of soot in combustion engines has become a major challenge for the motor vehicle sector in order to tackle the problems of air quality. The capacity to characterize soot whenever it is formed, directly in the combustion chamber of an engine, is currently one of the main challenges to be overcome in order to improve control of these pollutants.

In recent years, the technique for measuring particle size by LII (Laser Induced Incandescence), which is based on their laser-induced excitation, has emerged as offering the best potential in this area. However, to date, no evidence had been provided of its capacity to measure soot sizes in the specific conditions found in engines.

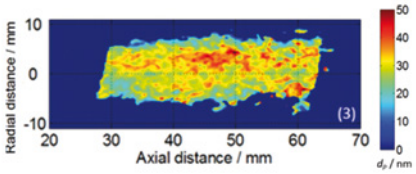
It was to this end that a research thesis conducted at IFPEN sought to examine in detail the active physical processes at work following laser-induced heating of soot, as well as the influence of environmental factors and, in particular, the high-pressure conditions specific to combustion chambers.

A theoretical approach was combined with experimental studies on various assemblies, ranging from simple laboratory flames to diesel jets during combustion, elucidating the physical phenomena involved[1].

This research led to optimal measurement strategies being defined for conditions representative of engines, followed by implementation of the first measurements in a diesel jet. The limitations of the technique were also clearly identified[2].

This original research concerning the use of LII will ultimately pave the way for more reliable measurements in engine environments.

Scientific contact:
gilles.bruneaux@ifpen.fr



Soot particle sizes in nm (color scale on the right) in a diesel jet during injection obtained by the LII technique.

(1) ***E. Cenker, G. Bruneaux,*** *T. Dreier, C. Schulz, Appl. Phys. B, 2015, 119, 745-763. DOI: 10.1007/s00340-015-6009-0*

(2) ***E. Cenker,*** *K. Kondo,* ***G. Bruneaux,*** *T. Dreier, T. Aizawa, C. Schulz, Appl. Phys. B, 2015, 119, 765-776. DOI: 10.1007/s00340-015-6106-0*

*Thesis entitled **"Imaging measurements of soot particle size and soot volume fraction with laser-induced incandescence at Diesel engine conditions".***

Appointment

Didier Houssin *was appointed Chairman of the French National Alliance for Energy Research Coordination (Ancre) in September 2015. IFPEN thus assumes the role for the second time, with the four founding members of Ancre taking it in turns to chair the body (CEA, CNRS, CPU and IFPEN). Through its global approach, Ancre helps to define the priorities of French public bodies in the field of energy research.*

Awards

• ***Luis Pereira de Oliveira*** *received the Excellence Award in Chemical Reaction Engineering from the European Federation of Chemical Engineering (EFCE) for his thesis on the development of a methodology for the compositional and kinetic modeling of refining processes, successfully applied in the hydrotreatment of diesel cuts and the hydroconversion of vacuum residues. His research has led to six publications in peer-reviewed journals and ten conference papers.*

• *For the fifth year running,* ***IFPEN*** *has earned a place in Thomson-Reuters' 2015 list of Top 100 Global Innovators. The innovation value of a company is assessed on the basis of four parameters: number of patents, patent-filing success rate, the international scope of the patents and, finally, the number of citations by other patents.*

IFPEN thesis prize

The 2015 Yves Chauvin prize has been awarded to Anthony Robert for his doctoral thesis on "Large-Eddy Simulation (LES) of abnormal combustion in downsized spark ignition engines". In this original thesis, LES was used for the first time to understand abnormal combustion in highly downsized spark ignition engines, which are subject to the more frequent development of damaging phenomena of this type.

HDR

• ***Stéphane Jay,*** *HDR at the Institut national polytechnique de Toulouse, for his research focusing on the "Digital simulation of dual-phase flows and reagents: developments and uses".*

Upcoming scientific events

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Sustainable Materials Inspired by the Living world: SMILE 2016 –*** *6-8 April 2016, IFPEN Rueil-Malmaison - www.rs-smile2016.com*

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Dynamics of Evolving Fluid Interfaces: DEFI –*** *12-13 October 2016, IFPEN-Lyon - www.rs-defi2016.com*

Publication

• *OGST – IFP Energies nouvelles journal – Issue 6, volume 70 (2015). The contributions to this issue have been classified into three groups: Enhanced Oil Recovery (EOR), asphaltenes and hydrates (http://ogst.ifpenergiesnouvelles.fr).*

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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