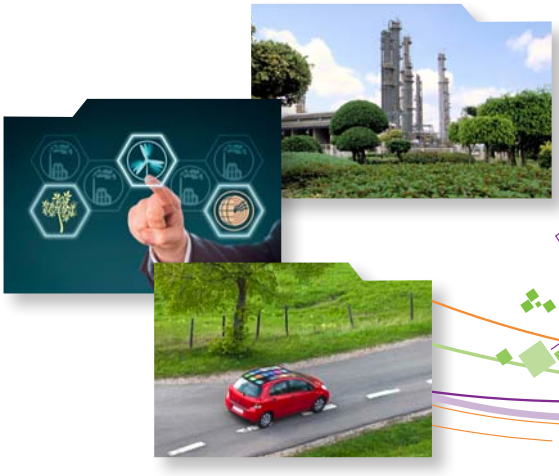

Science@ifpen

Issue 27 - December 2016

SPECIAL ISSUE
Publications by young researchers

This edition takes a look back at key results obtained by young researchers, PhD students and post-doctoral researchers, who have contributed to IFP Energies nouvelles' fundamental research. After a very full scientific career, I find it genuinely satisfying to note that this foundation is still full of life in order to provide new material for innovation. This also reflects the scientific vibrancy of our researchers, including highly committed supervisors and subject promoters, who are responsible for capitalizing on our results and maintaining fruitful relationships with our academic partners.

It is also a special pleasure for me to congratulate Kim Larmier, winner of the 2016 Yves Chauvin Prize, for his exemplary demonstration of the predictive power of ab initio *calculation, combined with micro-kinetic modeling, in an entirely ground-breaking multiscale approach linking the detailed small-scale description of active catalytic sites and the performance of a bio-based petrochemical process. The search for a Grail so close to my heart has thus not only been passed on, but has already started to produce great results.*

Our readers will also appreciate the wealth of other results presented in this edition, which meet the challenges of an IFPEN which is striving, now more than ever, to forge the energy of our future.

Hervé Toulhoat,
Executive Vice-President,
Scientific Management

2016 Yves Chauvin thesis prize

The 2016 Yves Chauvin Prize has been awarded to Kim Larmier for his doctoral thesis* defended in 2015 at the Pierre et Marie Curie University. His research has made it possible to understand and predict the properties of alumina-based catalysts used in the dehydration of a bio-based alcohol, isopropanol. The approach used by Kim Larmier brought together *ab initio* calculations, kinetic modeling and experimental measurements to understand this issue from the scale of reactive molecules to that of a catalytic reactor.

In the case of gamma-alumina, this approach helped, firstly, to identify the nature of the active site (Lewis acidic aluminum atoms), and secondly, to access the detailed reaction mechanism, thus allowing a predictive kinetic model to be constructed.

These results were set out in No. 25 of the scientific newsletter, Science@ifpen, published in July 2016.

The same approach has also been applied to the dehydration of isopropanol on alumino-silicates. The approach provided a very original method for determining the nature of the active site, with the synergic use of Brønsted and Lewis acids to accelerate the reaction. These results are currently in press in the prestigious journal *Angewandte Chemie, International Edition.*

*Thesis entitled **"Isopropanol conversions on alumina-based solids: a mixed experimental/multiscale modeling approach"**

IFP Energies nouvelles (IFPEN) is a major research and training player in the fields of energy, transport and the environment. From research to industry, technological innovation is central to all its activities.

Complex reactions? Supercritical microfluidics to the rescue!

Thesis by Bruno Pinho Da Silva*

Propylene is a key chemical intermediate produced through catalyzed selective hydrogenation of hydrocarbons (C3 fraction[a]). Studying the consequent reaction is complex as it is an extremely quick, triphasic (gas-liquid-solid) reaction. To better understand this reaction, studies aiming to improve the catalysts have been carried out in a single pellet string reactor, in supercritical phase[b].

This requires precise knowledge of the thermodynamic conditions (P,T) at which the real hydrocarbons/hydrogen mixes under study reach this supercritical state. Appropriate operating conditions can then be set to guarantee the desired state for the reactants within the reactor.

During this thesis, an original methodology for determining the "supercritical point" was successfully developed[1]. It is based on the use of a microfluidic device — high pressure and high temperature — on a silica/alumina chip, allowing thermodynamic data to be acquired quickly for a given reaction mixture.

After the mix to be tested has been injected into the chip, the temperature is increased at constant pressure until the boiling and dew points can be observed. The procedure is repeated at different pressures to obtain the range within which the mixture reaches its supercritical point.

In these operating conditions, studies using a single pellet string reactor have shown the intrinsic performances of the catalyst and provided a better understanding of the reaction system. Managing the gas/liquid mass transfer was thus revealed as a key for the productivity of the process.

This methodology, in addition to being appropriate for other industrial processes, has proven that the use of a microfluidic chip is a quick, precise and inexpensive means which can be used for determining other types of physico-chemical properties[2].

a - Mix of hydrocarbons composed of molecules containing three carbon atoms
b - Monophase intermediary state between gas and liquid

Microfluidic chip for determining supercritical conditions (P, T).

*Thesis entitled **"Specific properties of supercritical fluids for fast and exothermic reactive systems"**

(1) ***B. Pinho, S. Girardon, F. Bazer-Bachi, G. Bergeot,*** *S. Marre, C. Aymonier, Lab on a Chip 2014, 14 (19), 3843–3849.*
DOI: 10.1039/c4lc00505h

(2) ***B. Pinho, S. Girardon, F. Bazer-Bachi, G. Bergeot,*** *S. Marre, C. Aymonier, The Journal of Supercritical Fluids 2015.*
DOI: 10.1016/j.supflu.2015.04.016

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Have we solved the mystery of the sedimentary "black boxes"?

Thesis by Vincent Crombez*

The hydrocarbons produced by the oil industry come from source rocks, rocks that are rich in organic matter. In contrast with the traditional view, it has recently been shown that these source rocks are extremely heterogeneous. It is therefore necessary to implement new integrated approaches to meet the needs of the upstream oil sector. These approaches aim to combine the characterization and modeling of such heterogeneities (cf. figure) in order to better identify the resources available for production.

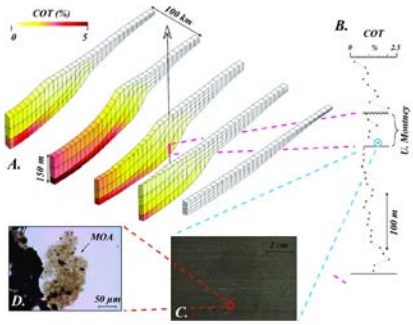
This thesis, centered on marine sedimentary basins, aimed to define and implement a multi-disciplinary methodology from pore to basin scale, in order to characterize, conceptualize and model these source rocks. This has been made possible through the use of thousands of both continuous and representative data on source rocks.

In addition to the significant data collection and handling work, this workflow used know-how from geochemistry, sedimentology and stratigraphy, as well as basin modeling.

This methodology, which has been developed and tested on the West Canadian basin (Trias, Montney and Doig formations), has already provided a robust model capable of rendering the architecture and heterogeneities of this source rock[1, 2]. These results have helped improve IFPEN's basin modeling tools.

New research areas include the small-scale study of the mechanisms governing the generation and expulsion of hydrocarbons from source rocks. A more detailed description of these areas also allows us to envisage a better understanding of changes to the climate and oceanic dynamics on a geological time scale[2].

*Thesis entitled **"Petrofacies, sedimentology and stratigraphic architecture of rocks rich in organic matter"**



Various modeling and characterization aspects used in this work.
A. Stratigraphic modeling of the distribution of organic matter.
B. Analysis of Rock Eval 6 to calibrate the model.
C. Facies rich in organic matter.
D. Organic particles.

*(1) **V. Crombez, S. Rohais, F. Baudin,** T. Euzen, accepted for Bulletin of Canadian Petroleum Geology.*

*(2) **V. Crombez, F. Baudin, S. Rohais,** L. Riquier, T. Euzen, **S. Pauthier,** B. Caron, N. Vaisblat, accepted for Marine and Petroleum Geology.*

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Urban Traffic: Green lights for eco-travel

Thesis by Giovanni De Nunzio*

Optimal adaptation of driving to urban traffic conditions could help reduce energy consumption and polluting emissions, as well as traffic jams. Several situations could therefore be improved, such as turning a succession of tri-colored traffic lights to green as soon as the vehicle exchanges information with the control infrastructure to know in advance the sequences of these signals.

Being able to determine in real time the instruction to be given to the driver will help obtain the speed profile, thus avoiding stopping at the traffic lights, while limiting the energy consumption and travel time.

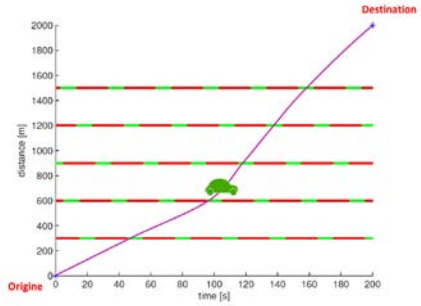
This is non-linear and non-convex optimization problem which takes a very long time to calculate and is difficult to resolve.

An alternative, three-step method was developed as part of this thesis[1, 2]. The first step is to reduce the space of possible solutions by considering the minimum and maximum speeds between two successive sets of traffic lights. The possible speed profiles are then approximated using tools derived from graph theory. Resolving this convex optimization problem should make it possible to find the most appropriate speed profile.

This marginally sub-optimal method provides a response in around one second, versus one hour to calculate the optimum speed using a traditional approach. The simulations carried out also show fuel savings of around 20% as well as an average reduction in journey time of around 4%.

It will be possible to use this calculation strategy for other issues regarding sustainable travel, such as improving the energy efficiency of vehicles, driving delegation and, in the longer term, self-driving vehicles.

*Thesis entitled "**Traffic Eco-Management in Urban Traffic Networks**"



Example of journey calculated to avoid stopping at five successive traffic lights.

(1) ***G. De Nunzio,*** *C. Canudas de Wit,* ***P. Moulin, D. Di Domenico,*** *International Journal of Robust and Nonlinear Control, 2015, 26, (6), 1307-1324. DOI: 10.1002/rnc.3469*

(2) ***G. De Nunzio,*** *G. Gomes, C. Canudas de Wit, R. Horowitz,* ***P. Moulin,*** *IEEE Transactions on Control Systems Technology, 2016. DOI: 10.1109/TCST.2016.2577002*

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Characterizing foams using microfluidics

Post-doctoral work by Cyril Micheau*

The formation, flow and stability of foams are important in numerous processes, such as Enhanced Oil Recovery (EOR[a]), where foam is used to control the flow of fluids injected into porous areas with varying permeability.

Understanding and controlling the behavior of foams in confined medium is essential for optimizing these processes. Such understanding and control is achieved by developing observation and analysis techniques to identify and quantitatively describe the involved phenomena. In this context, microfluidics helps both to generate a very controlled foam and then confine it to a relevant scale (10 µm to 1 mm), and all this while visualizing and quantifying the flows and changes in morphology.

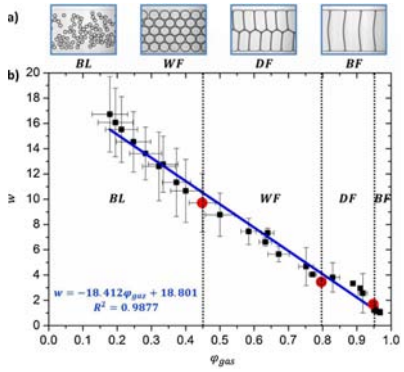
The experimental work carried out as part of this study looked at model foams whose stability can be modified using pH and surface viscosity. By using microsystems of appropriate geometry, the work linked a foam's structure to the degree of confinement of its bubbles (cf. figure) and showed the impact of physical-chemistry on its flow[1].

This work also confirmed the potential of microfluidics for acquiring quantitative data, with a view to providing data for flow simulators or helping in the choice of formulations.

The developed methodology, enhanced by analysis techniques[b], could be used to study other factors met in real environments, such as salinity or the presence of oil, and it may also be used for other complex systems[c].

a - Enhanced Oil Recovery
b - Nuclear Magnetic Resonance
c - Emulsions, suspensions, polymers in solution, etc.

*Post-doctoral research entitled "**Characterization of foams in an EOR context**"



a) Type of structure
b) Diagram of foam phase
w: confinement
ϕgas: gas surface fraction

(1) ***C. Micheau, E. Rosenberg, L. Barré, N. Pannacci,*** *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016, 501, 122–131. DOI: 10.1016/j.colsurfa.2016.04.061*

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Combining models for better separation

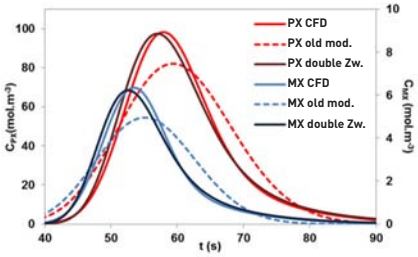
Thesis by Leonel Fangueiro Gomes*

The chromatographic separation processes called simulated moving bed (SMB), used in the chemical and agribusiness industries, rely on multiple beds containing the adsorbent, so as to produce a countercurrent flow between the liquid and solid phases. However, the hydrodynamics within such adsorption columns, which themselves are made of multiple beds and distributors, have an important impact on the global efficiency of the separation.

Modeling has a crucial role to play in assessing this impact with precision and developing technologies suitable for new absorbents. However, CFD[a] tools are not appropriate for simulating processes such as SMB due to the complex nature of the hydrodynamics. A new methodology has thus been developed as part of this thesis to handle this complexity whilst ensuring the simulation times remain reasonable.

Starting from stationary CFD simulations of industrial adsorbents, internal age distribution transport theory[b] was used to develop and validate a 1D multi-entry, multi-exit model called the Double Zwietering model[c]. This hydrodynamics model is twinned with the mass transfer model and takes into account the adsorption isotherms, without it impacting too heavily on the calculation times [1]. It therefore provides more precise simulation of the experimental results (cf. figure) for SMB-based processes[2], paving the way for the development of new bed and distributor geometries.

This methodology is already in use at IFPEN for other applications, such as moving bed reactors.



Results of drilling simulation[d] with reference model (CFD), old model and new model: profiles for p-xylene (PX) and m-xylene (MX).

a - Computational Fluid Dynamics
b - A theory determining, at each observation point in the system, the distribution of the time taken for the molecules situated at these points to arrive there
c - Known by this name as it is based on the theoretical concepts of degrees of mixing developed by Danckwerts and Zwietering in the 1960s
d - Experiment following the exit composition of an adsorbent bed where the composition of input was varied on entry

*Thesis entitled **"Study combining hydrodynamics and adsorption for simulated moving bed (SMB) applications"**

(1) ***L. Gomes, F. Augier, D. Leinekugel-Le-Cocq**, I. Vinkovic, S. Simoëns, Chemical Engineering Science, 2015, 132, 46-58. DOI: 10.1016/j.ces.2015.04.019*

(2) ***L. Gomes, F. Augier, D. Leinekugel-Le-Cocq**, I. Vinkovic, S. Simoëns, Chemical Engineering Science, 2016, 153, 188-198. DOI: 10.1016/j.ces.2016.07.027*

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News

• *The ANCRE alliance, chaired by Didier Houssin, organized a colloquium entitled "COP 21 One Year On: 19 R&I bodies and academics committed to the energy transition", which saw 150 attendees come together on 25 November 2016. www.allianceenergie.fr*

• *Together with 11 partners, IFPEN launched the consortium to create the OQUAIDO chair in applied mathematics — from "Optimisation et QUAntification d'Incertitudes pour les Données Onéreuses" in French — with the aim of resolving problems concerning uncertainty propagation, sensitivity analysis, optimization, inversion and calibration.*

Awards

• ***Céline Chizallet** was joint-winner of the 2016 Young Researcher Prize awarded by the Chemistry and Physics Division (DCP), jointly run by SCF - French Chemistry Society and SFP - French Physics Society.*

• ***Giovanni De Nunzio,** was awarded the 2016 Thesis Prize by the Grenoble Alps Community of Universities and Institutions (COMUE) for the scientific excellence of the work carried out as part of his thesis on "Eco-Management of Traffic in Urban Networks". (see article on previous page)*

HDR

• ***Loïc Barré** was awarded an HDR at Pierre et Marie Curie University for his work on "From Mesoscopic Structure to Macroscopic Properties: applications in several systems of interest to the oil industry".*

Upcoming scientific events

• *The IFP Energies nouvelles Scientific Conference **– Computational chemistry to reduce atmospheric pollution –** 13 and 14 March 2017, IFPEN Rueil-Malmaison – www.rs-compchemistry.com*

• ***DEPOS27: deformation of solid polymers –** 22 to 24 March 2017, Dourdan, France – www.depos27.fr*

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