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SPECIAL ISSUE
Recent PhD graduates

The aim of fundamental research at IFPEN, structured around cross-functional and multidisciplinary scientific questions, is to build the skills and knowledge base required for the development of new solutions in the fields of energy, transport and climate. The contribution made by these PhD students is an essential component of such research and illustrates our productive collaboration with academic research partners, in France and around the world.

Each year, IFPEN hosts around forty PhD students who will train in research while channelling their expertise and enthusiasm into addressing major scientific challenges, and identifying potential solutions with concrete applications.

For many years now, IFPEN's Scientific Board has been awarding the Yves Chauvin prize to the best thesis defended. By presenting a synopsis of each of the theses short-listed for the 2018 award, this special issue highlights the richness of themes and disciplinary fields covered. This year, the prize was awarded to Aurélie Pirayre, for her PhD on bioinformatics, embodying the capacity of these young researchers to build creative bridges between scientific fields.

I hope you enjoy reading this issue.

Benjamin Herzhaft,
Fundamental research program manager in the Scientific Division

"BRANE Power": of genes and algorithms, an alliance for green chemistry

Thesis by Aurélie Pirayre*, 2018 Yves Chauvin prize

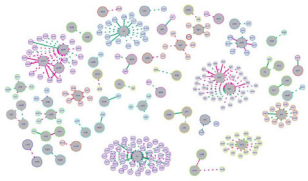
Trichoderma reesei is a fungus that is being studied at IFPEN for its enzyme production used in 2nd-generation biofuel production processes[a]. A more accurate understanding of its genetic mechanisms is required in order to improve the efficiency of such processes. Hence, the purpose of this thesis was to identify the way in which their genes interact – directly or otherwise – in connection to enzyme production.

Biological data to be analyzed for this type of research possess a considerable volume and significant heterogeneity. They require the development of efficient bioinformatic[b] algorithms.

An optimization tool suite, based on biological and structural constraints, was developed to construct gene interaction graphs. Hinged around the BRANE[c] concept, this suite includes BRANE Cut[1], a method dedicated to regulatory networks (Figure), and BRANE Clust[2] adding, to networks, gene clustering on the basis of their biological functions.

The improvement, with respect to published reference methods, was demonstrated, via benchmark datasets[d], on model microorganisms. Upon validation, BRANE was employed on Trichoderma reesei, with a meticulous and promising selection of candidate genes.

These new tools provide invaluable aid in rapidly identifying useful interaction cascades for enzyme production. Broadening the scope becomes reachable. This involves the alliance of new "omic" data and epigenetic mechanisms, extended to the lineage of our fungus.



***Gene network of the model microorganism* Escherichia coli *obtained with BRANE Cut*[1].**

*Thesis entitled « **Reconstruction and Clustering with Graph optimization and Priors on Gene networks and Images** »

a - Only using the non-edible parts of the plants.
b - Using the storage and analysis power of information technology to study life science fields.
c - Biologically-Related Apriori Network Enhancement.
d - Both real and simulated, made available by the DREAM consortium (http://dreamchallenges.org/).

(1) ***A. Pirayre, C. Couprie, F. Bidard,*** *L. Duval, J-C. Pesquet. BMC Bioinformatics, 2015. DOI: 10.1186/s12859-015-0754-2*

(2) ***A. Pirayre,*** *C. Couprie,* ***L. Duval,*** *J-C. Pesquet. IEEE/ACM Transactions on Computational Biology and Bioinformatics, 2018. DOI: 10.1109/TCBB.2017.2688355*

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Improving the simulation of the transport process in nanopores using molecular dynamics

Thesis by Pauline Simonnin*

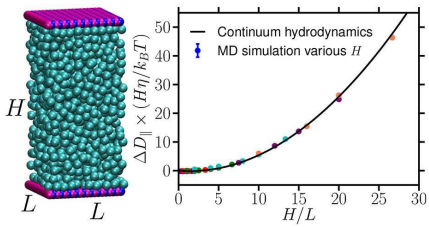
Understanding and modeling transport processes in highly confined media is a major challenge in order to innovate in the broad range of applications covered by research conducted at IFPEN: catalyst design, electricity storage and generation, sealing solutions for geological storage. In the latter area, the use of molecular dynamics made it possible to simulate the diffusion of water and gas molecules in clay nanopores.

This research benefited from the high-performance computing resources provided by GENCI[a] . During the simulation, a strong dependance of the diffusion coefficients obtained on the size and shape of the simulation box was demonstrated (figure). This spurious artefact is due to the hydrodynamic interactions that arise, numerically by the imposed periodic boundary conditions, equivalent to consider an infinite set of replicas of the original system. A complex analytical calculation made it possible to quantify and correct it using an explicit formula[1]. The excellent agreement between theory and numerical experiments confirms the origin of the correction, and may be use practically.

The study of clay interface diffusion highlighted the effect of ionic species, always present in the fluid, on the structure and hydrodynamic properties of these interfaces[2]. Its incorporation makes calculations aimed at reproducing the diffusion phenomenon more realistic and improves their predictive capacity.

This research demonstrated the contribution of molecular dynamics tools to the acquisition of quantitative property predictions used for the simulation of transport processes in nanoporous media. The injection of these results into transport models on a larger scale opens up avenues of potential interest in the energy, chemicals and environmental sectors.

a - National high-performance computing resource.



Apparent diffusion coefficient as a function of the shape of the simulation box: excellent correlation between the analytical formula - solid line - and simulations for different couples (H, L).

(1) *P. Simonnin, B. Noetinger, C. Nieto-Draghi, V. Marry & B. Rotenberg.*
DOI: 10.1021/acs.jctc.7b00342

(2) *P. Simonnin, B. Noetinger, C. Nieto-Draghi, V. Marry & B. Rotenberg. (2018). The Journal of Physical Chemistry C.*
DOI: 10.1021/acs.jpcc.8b04259

*Thesis entitled **"Fluid transport in nanopores: from molecular models to continuous models"***

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NMR and Raman imaging: impregnation of catalysts as if you were there

Thesis by Leonor Catita*

In order to obtain cleaner fuels, hydrotreatment (HDT) processes require new, more active and more selective catalysts. In turn, this necessitates a better understanding of a key step in the preparation of catalysts: impregnation of the support by an aqueous or organic solution of the metallic precursors, future active sites in catalysis.

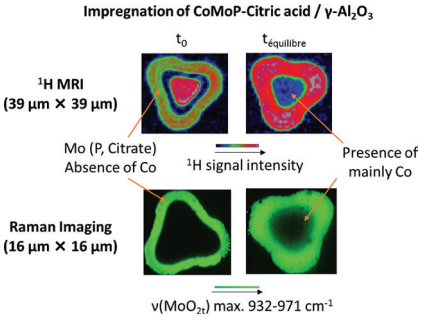
In this research, an analytical methodology based on MRI[a] and Raman[b] techniques was developed to characterize the impregnation step. The objective is to be able to describe the physical and chemical phenomena involved in the transport of the metallic precursor within the support porosity.

This study marked the first in situ use of MRI in real systems such as HDT catalysts to monitor the impregnation step with a complex aqueous solution[c], in the presence or otherwise of citric acid[1]. Thanks to Raman imaging, we confirmed the identification of the chemical characteristics of the molybdenum species deposited on the support. We thus highlighted a preferential affinity between citric acid and the surface of the γ alumina (figure), as well as the significant impact of the local pH and the presence of phosphorus on the characteristics of the species deposited[2].

These results were used as the foundations for developing a mathematical model aimed at rationalizing the monometallic catalyst impregnation step. The model is used to estimate, for a given solution, the impregnation time within new supports and to evaluate active phase accessibility.

The method developed can be applied to numerous other catalyst systems, in order to make them more efficient via the improved distribution of the active phase.

a - NMR (Nuclear Magnetic Resonance) Imaging.
b - Spectroscopic method providing information about chemical structure and compounds present.
c - Composed of molybdenum (Mo), cobalt (Co) and phosphorus (P).



Effect of the presence of citric acid in HDT catalysts ($CoMoP/\gamma\text{-}Al_2O_3$).

*Thesis entitled **"Contribution of NMR and Raman imaging for modeling and rationalization of the impregnation process of metallic precursors in porous media"***

(1) *L. Catita, A-A. Quoineaud, D. Espinat, C. Pichon, O. Delpoux, Applied Catalysis A:General 547 (2017), 164-175.*
DOI : 10.1016/j.apcata.2017.08.039

(2) *L. Catita, A-A. Quoineaud, M. Moreaud, D. Espinat, C. Pichon, O. Delpoux, Topics in Catalysis.*
DOI : 10.1007/s11244-018-1038-7

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Lacustrine sedimentary series: an archive of past environmental changes to better understand the present

Thesis by Alexandre Lettéron*

Deciphering environmental changes and their impacts on ecosystems is one of the major challenges facing our modern societies.

In this respect, due to fluctuations in their level and very rapid ecological variations[a], lacustrine sedimentary systems constitute particularly comprehensive and accurate records of the evolution of environmental parameters (figure) over geological timescales. However, a problem concerns the identification and ranking of these parameters in terms of impact, in order to build predictive models. These models will be used to quantify the evolution of lacustrine systems, in terms of water hydrology, ecology and geochemistry (salinity, alkalinity, etc.).

The thesis focused on combining – something that is rarely done – sedimentological, palaeontological, palaeobotanical and geochemical approaches for the characterization of lacustrine sedimentary series[(1)], dating back to the Priabonian era, in South-East France. This was a key period in the history of the Earth, heralding the start of the EOT[b]: the last major climate crisis of the past 50 million years.

This research demonstrated the impact of the pre-crisis climatic instability on the ecosystem[(2)]. Its results provide some of the keys to understanding and modeling environmental problems such as the eutrophication[c] and salinization of continental water bodies.

They will be incorporated into ongoing reflection processes at IFPEN in order to refine stratigraphic modeling and adapt them to current environmental problems.

*Thesis entitled **"Sedimentological, stratigraphic and paleoenvironmental characterization of the variable salinity lacustrine carbonate system of the Alès Basin and bordering regions (Priabonian, S-E France): paleoclimatic and paleogeographic implications"**

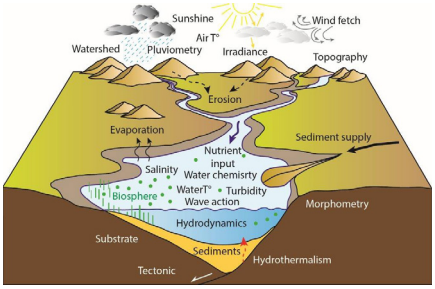

Diagram illustrating some control parameters for a lacustrine system.

a - Due to their generally closed character and their small size with, among other things, water that is highly variable chemically.
b - Eocene-Oligocene Transition (or *"Grande coupure"*, i.e., "Great Break").
c - Excessive accumulation of nutrients (P, N, K) in the aquatic system.

(1) ***A. Lettéron,*** *F. Fournier,* ***Y. Hamon****, L. Villier, J-P. Margerel, A. Bouche, M. Feist,* ***P. Joseph,*** *2017. Sedimentary Geology, 358, pp. 97–120. DOI: 10.1016/j.sedgeo.2017.07.006*

(2) ***A. Lettéron, Y. Hamon,*** *F. Fournier, M. Séranne, P. Pellenard,* ***P. Joseph,*** *2018. Sedimentary geology, 367, pp. 20-47. DOI: 10.1016/j.sedgeo.2017.12.023*

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Power in unity: a new approach to simulate complex flows

Thesis by Mohamed Essadki*

Gas-liquid two-phase flows lie at the heart of numerous industrial applications[a] for which numerical simulation is a dimensioning and optimization support tool. Such simulation must be predictive with reasonable calculation costs.

While monophase flow simulation already meets these requirements, the same cannot be said for the two-phase scenario. In the injection field, in particular, flow topology is highly complex, with different zones[b] with a high level of interactivity. The latter are described by different physical models that cannot be easily combined later, making it difficult to construct predictive models that can be used for industrial-scale simulations.

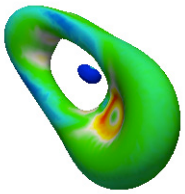
The research consisted in seeking an original unified approach to describe all these flow topologies. The method employed focused on:

- interface statistics to identify new geometric variables valid in all flow regimes[(1)];
- advanced numerical analysis making it possible to implement these variables in a Eulerian[c] flow model[(2)];
- algorithmic geometry to calculate these variables in flow DNS[d] (figure) in order to propose the first closures[e] for the model.

This new model, incorporated in a parallel 3D simulator, demonstrated its robustness and reasonable cost on a first set of jet simulations.

The thesis' second contribution resides in a fine-scale gas-liquid interface analysis tool that can be used to characterize the results of DNS-type calculations. Its use will make it possible to improve averaged larger-scale models, proposing new closures.

*Thesis entitled **"Contribution to a unified Eulerian modeling of fuel injection: from dense liquid to polydisperse evaporating spray"**



Droplet deformation in a direct two-phase simulation.

a - For example: injection process in the automotive and aeronautics sectors, chemical engineering processes.
b - A dense liquid core, droplets and filaments of all forms.
c - A Eulerian model simulates the continuous liquid phase, in contrast to a particle or droplet model.
d - Direct Numerical Simulation.
e - Estimations by physical and numerical experiments of model terms that cannot be calculated directly.

(1) ***M. Essadki, S. de Chaisemartin,*** *M. Massot, F. Laurent, A. Larat &* ***S. Jay.*** *OGST. DOI: 10.2516/ogst/2016012.*

(2) ***M. Essadki, S. de Chaisemartin,*** *L. Drui, F. Laurent, M. Massot. SIAM J. Appl. Math. DOI: 10.1137/16M1108364.*

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Shedding new light on the geological history of sedimentary basins thanks to thermochronometry

Thesis by Xavier Mangenot*

Determining the temperature conditions of past geological episodes is a major challenge for research in geosciences. The interest lies in the fact that they govern the physical and mechanical properties, as well as the chemical reactivity of geological materials and determine the formation of underground energy resources.

Since the 1960s, the reconstitution of the thermal history of sedimentary basins has been largely based on the chemical and physical properties of the organic matter present in sediments and then of mineral markers, with varying degrees of reliability.

Over the past few years, two promising isotopic tools have emerged: the Δ_{47} thermometry and the U-Pb chronometry using LA-ICP-MS[a]. They make it possible to determine, respectively, the absolute temperature and age of crystallization of carbonate minerals with an unprecedented degree of accuracy[1, 2].

This thesis combined them in a new approach called Δ_{47}/(U-Pb) carbonate thermochronometry[3], furnishing more accurate contraints for basin modeling thermal calibration.

Tested on the Paris Basin, this approach was used to directly and accurately reconstruct the time-temperature evolution of a geological layer over more than 150 million years (figure). Due to its performance and ease of use, this technique represents a small revolution in the field of geosciences for the study of sedimentary basins.

a - Inductively coupled plasma mass spectrometry, with laser ablation.

*Thesis entitled **"Pairing Δ_{47} thermometry and U/Pb chronometry to reconstruct the diagenetic, thermal and fluid-fow histories of carbonate rocks in sedimentary basins: case of the Paris basin"**

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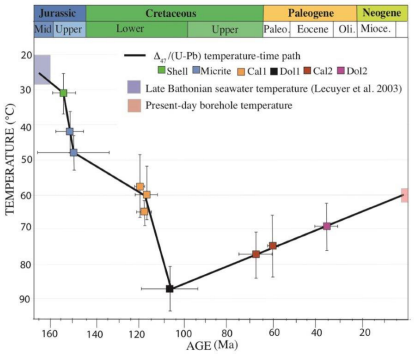


Reconstructed thermal history via the combination of Δ_{47} temperatures (y-axis) and U-Pb ages (x-axis).

(1) ***X. Mangenot, M. Gasparrini, V. Rouchon,*** *M. Bonifacie (2018), Sedimentology. DOI :10.1111/sed.12427*

(2) ***X. Mangenot,*** *M. Bonifacie,* ***M. Gasparrini,*** *A. Götz, C. Chaduteau, M. Ader, V. Rouchon (2017), Chemical Geology. DOI: 10.1016/j.chemgeo.2017.10.011*

(3) ***X. Mangenot, M. Gasparrini,*** *A. Gerdes, M. Bonifacie,* ***V. Rouchon,*** *2018 Geology. DOI: 10.1130/G45196.1*

Catalyst selectivity: spectral investigations

Thesis by Fabien Caron*

The environmental constraints associated with the production of high-octane sulfur-free gasolines require improvements to the selectivity of the catalysts used for the hydrodesulfurization (HDS) of sulfur-containing molecules[a]. Given the scale of this industrial challenge, it is vital to improve the understanding of the reaction mechanisms governing this selectivity on an atomic scale.

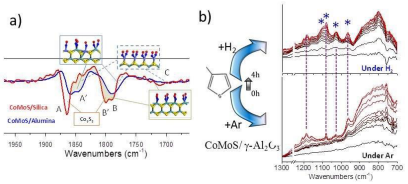
Thanks to kinetic studies via high-throughput experimentation, the hypothesis of a support effect on the function of active phase[b] sites was confirmed: the selectivity of the CoMoS catalyst is different depending on the nature of its support (alumina-gamma, alumina-delta or silica).

A multi-technical approach combining high-resolution microscopy, infrared spectroscopy (figure) and ab initio modeling[c], was used to explain this fact. It is due to the impact of the support on the nanostructure of the active CoMoS phase and on speciation[d] of the promoted sites.

The design of a dedicated unit, combining gas chromatography and in situ IR, then made it possible to explore, for the first time, the formation of intermediates on the catalyst in conditions similar to those of the industrial process.

This research, conducted in partnership with Turin University, paved the way to the development of an innovative and promising methodology for innovative operando catalyst characterization.

a - While limiting the hydrogenation of alkenes (unsaturated hydrocarbons with formula C_nH_2), to maintain the octane number.
b - In this case molybdenum disulfide, promoted by cobalt (CoMoS).
c - Based on basic laws of physics.
d - Chemical and structural form in which an element is found.



IR spectroscopy techniques employed:
a) IR spectra of CoMoS/silica and /γ-alumina saturated in NO[1].
b) In situ ATR-IR monitoring of the interaction of 3-methylthiophene on CoMoS/γ-alumina[2].

*Thesis entitled **"Bridging the gap between spectroscopic and catalytic properties of supported CoMoS catalysts"**

(1) ***F. Caron, M. Rivallan, S. Humbert, A. Daudin,*** *S. Bordiga,* ***P. Raybaud.*** *J. Catal. 361 (2018) 62. DOI: 10.1016/j.jcat.2018.02.017*

(2) ***F. Caron, M. Rivallan, A. Daudin,*** *S. Bordiga,* ***P. Raybaud*** *(in progress)*

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