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A thesis is the culmination of a long study program and forms a solid foundation from which to launch a career in the world of academic or industrial research. Every year, IFP Energies nouvelles (IFPEN) plays host to around 40 PhD students working across its various research sectors. Our doctors are trained in scientific methods and are familiar with the most advanced state of the art in the field of the thesis. They are aware of the requirements of applied research and have a sound general knowledge of the energy sector as a whole. These factors combine to make them move seamlessly into the job market.

Each year, IFPEN Scientific Board awards the Yves Chauvin prize to the best thesis defended. This year the prize has been jointly awarded to Ibrahim Abada for his research in the field of natural gas markets in Europe and to Marie Savonnet for her work on the synthesis of new catalysts based on MOFs. The Scientific Board praised the exceptional quality of their research, their major scientific contribution and their very significant potential industrial impacts. This issue takes a close look at the 6 finalists, selected from 14 applicants for the prize.

We hope that you enjoy this issue.

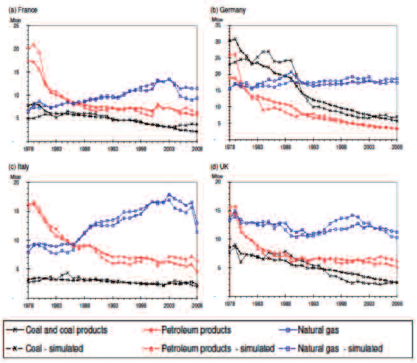
Andreas Ehinger,
Director of Doctoral Studies

A GaMMES model for the gas industry

Thesis by Ibrahim Abada, 2012 Yves Chauvin prize-winner

Modeling the future of the European natural gas sector poses some real challenges. Indeed, the natural gas industry is governed by two essential features: it is an extractive industry and it is a network industry. In addition, one may wish to represent the interplay of three other concomitant phenomena:
- on the demand side, there is a complex adjustment dynamics of consumption in reaction to fuel prices because inter-fuel substitutions substantially matter in the long-run, but not in the short-run;
- imperfect competition resulting from oligopolistic behavior is observed all along the value chain;
- different intermediation schemes coexist between the upstream and the downstream parts of the value chain (long-term contracts, short-term markets).

This PhD thesis aimed at developing an original modeling approach adapted to the economics of the natural gas industry. It was performed in a close partnership with EDF R&D and with the University of Maryland. On the demand side, the thesis proposes an enhanced functional specification using a system dynamics-based model. This dynamic functional specification of the demand function for natural gas can be used in an imperfect competition model. On the supply side, the thesis details an innovative oligopolistic model based on generalized Nash-Cournot equilibriums. The model explains the coexistence of long-term contracts and short-term markets. The combination of these two core components led to the creation of the GaMMES model, paving the ways for a better understanding of the strategic behaviors observed in this industry.



Comparison of historical and simulated consumption levels in France, Germany, Italy and the UK.

I. Abada, O. Massol, Security of supply in the European Gas Market. A model-based analysis, *Energy Policy, 2011, 39 (7), 4077-4088. DOI: 10.1016/j.enpol.2011.03.043*

I. Abada, *S. Gabriel, V. Briat,* ***O. Massol,*** A Generalized Nash–Cournot Model for the Northwestern European Natural Gas Markets with a Fuel Substitution Demand Function: The GaMMES Model, *Networks and Spatial Economics, 2012. DOI: 10.1007/s11067-012-9171-5*

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Gaining a better understanding of carbonate reservoirs

Thesis by Mickaël Barbier

The characterization and modeling of carbonate reservoirs is one of the oil industry's main concerns. However, these reservoirs have petrophysical properties that are difficult to predict. This is because the intrinsic heterogeneities of carbonate systems are further compounded by heterogeneities linked to the geological history of the sediment (diagenesis, fracturing).

Until now, a lack of understanding of the control factors governing the petrophysical properties and the distribution of fracturing in these fractured carbonate reservoirs has been a major obstacle.

As part of this thesis, based on fine characterization of sedimentary facies, diagenesis and fracturing, the factors controlling fracturing distribution and parameters have been identified and integrated into a system for the joint stochastic simulation of "facies and diagenesis". The case study used was the Madison carbonate formation (Wyoming, United States).

Aerial view of one of the reservoirs studied.

The research has revealed, first of all, that sedimentary dynamics and early diagenesis have a direct effect on mechanical fracturation and, secondly, that the structural style controls the intensity of fractures.

These results will serve as a reference for the construction of specific case studies dedicated to fractured carbonate reservoirs for CobraFlow™ and FracaFlow™ software developed by IFPEN.

M. Barbier, Y. Hamon, B. Doligez, *J.-P. Callot, M. Floquet,* ***J.-M. Daniel,*** Stochastic Joint Simulation of Facies and Diagenesis: A Case Study on Early Diagenesis of the Madison Formation (Wyoming, USA), *OGST, 2012, 67, 123-145.*

M. Barbier, Y. Hamon, *J.-P. Callot, M. Floquet,* ***J.-M. Daniel,*** Sedimentary and diagenetic controls on the multiscale fracturing pattern of a carbonate reservoir: The Madison Formation (Sheep Mountain, Wyoming, USA), *Marine and Petroleum Geology, 2012, 29, 50-67.*

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How asphaltenes aggregate

Thesis by Joëlle Eyssautier

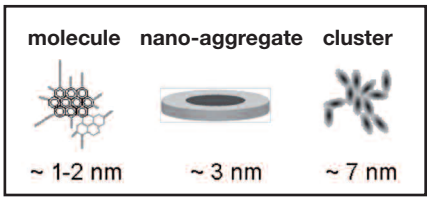
Driven by the growing demand for fuels and the increasing rarity of light crude oil supplies, there is a need to fully understand heavy oil hydroconversion processes. These heavy feeds are characterized by high concentrations of functionalized aromatic species with a high boiling point: asphaltenes.

In solution, the latter form aggregates as a result of mechanisms that are as yet poorly understood. This aggregation in heavy feeds, in reactional conditions, is still little described given the complexity of the products and the operating parameters. Yet the phenomenon appears to limit the diffusion of these species in the nanoporous network of catalysts and, consequently, their conversion.

The research for this thesis first focused on the self-association properties of asphaltenes in simple solvents. To this end, simultaneously static and dynamic radiation-scattering probes were used. This approach made it possible to model the phenomenon: asphaltenes form permanent aggregates[1] organized in a hierarchical manner *(see Fig.)*. Molecules presenting polycondensed aromatic structures and peripheral alkyl chains are stacked on top of one another to form disc-shaped nano-aggregates[2]. These then join together on a larger scale to form loose clusters, explaining the high viscosities of asphaltenic crude oils[3].

This description was then extended to temperature conditions close to those found in hydrotreatment processes. It was observed that, in this case, the clusters split up, but the nano-aggregates persisted up to 300°C [4].

These results will make it possible to improve the design of catalysts, and also to examine the interfacial behavior of asphaltenes, a key factor in the adsorption, wettability and stability of oil emulsions.



Hierarchized organization of asphaltene molecules.

(1) ***J. Eyssautier, D. Frot, L. Barré,*** *Langmuir, 2012, 28, 11997–12004. DOI: 10.1021/la301707h*

(2) ***J. Eyssautier,*** *P. Levitz,* ***D. Espinat,*** *J. Jestin, J. Gummel, I. Grillo,* ***L. Barré,*** *J. Phys. Chem. B., 2011, 115, 6827–6837. DOI: 10.1021/jp111468d*

(3) ***J. Eyssautier, I. Hénaut,*** *P. Levitz,* ***D. Espinat, L. Barré,*** *Energy & Fuels, 2012, 26, 2696–2704. DOI: 10.1021/ef201412*

(4) ***J. Eyssautier, D. Espinat,*** *J. Gummel, P. Levitz, M. Becerra, J. Shaw,* ***L. Barré,*** *Energy & Fuels, 2012, 26, 2680–2687. DOI: 10.1021/ef201411r*

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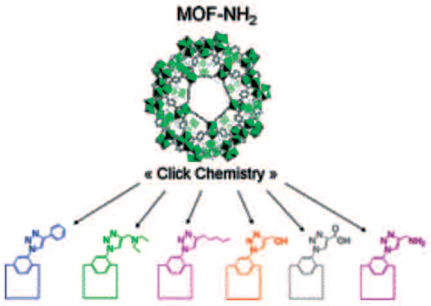
Functionalization of MOFs

Thesis by Marie Savonnet, 2012 Yves Chauvin prize-winner

MOFs (Metal Organic Frameworks) are hybrid materials combining metal cores with organic ligands. This new class of porous solids, often compared to zeolites, is highly versatile: the physicochemical properties of MOFs can be custom-regulated, depending on the choice of the "clusters" (the metal) and the "linkers" (the organic ligands). It is thus possible to obtain materials with a very high surface area and porosity, or materials with specific chemical functions at their surface.

This thesis focuses on the design of functionalized MOFs. Thanks to the development of an original functionalization method (using Click Chemistry) and the high level of versatility of MOFs, new avenues are being identified for the design of heterogeneous catalysts, with control of structural (porosity, surface area, thermal stability) and chemical (acidity, alkalinity, polarity) properties.This method, which can be applied to all MOFs carrying a $-NH_2$ function, consists in coupling an azide function with an alkyne one. Functionalization of numerous MOFs using a broad variety of organic species is therefore possible. The figure below illustrates the principle of the method, as well as the diversity of materials obtained. These new systems have undergone an initial evaluation in the field of transesterification catalysis. This evaluation demonstrates that the use of functionalized MOFs via access to solids with specific functions may make it possible to develop new catalysts, for fine chemistry reactions such as enantioselective catalysis, or emerging applications such as photocatalysis.This thesis research has led to 8 patent applications and numerous publications as well as papers at national and international conferences.



Strategy to functionalize MOFs using a Click Chemistry reaction.

M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel, D. Farrusseng, J. Am. Chem. Soc., 2010, 132 (13), 4518.

M. Savonnet, E. Kockrick, A. Camarata, D. Bazer-Bachi, N. Bats, V. Lecocq, C. Pinel, D. Farrusseng, New J. Chem., 2011, 35, 1892.

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Trichoderma reesei: it's all in the genes

Thesis by Thomas Portnoy

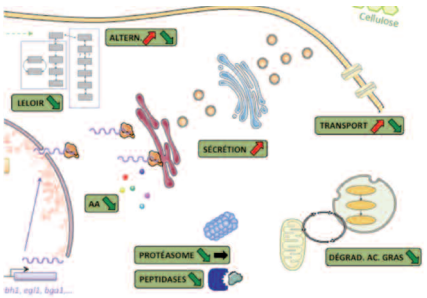
The production of 2nd-generation bioethanol is based on the action of enzymes, derived from the filamentous fungus *Trichoderma reesei*. The enzymes are obtained by cultivating the fungus in a fermenter. The cost of this type of culture is still very high. One of the avenues being explored to bring down the cost is improving the performance of *T. reesei* strains through genetic engineering.

The challenge is to identify which of the organism's several thousand genes need to be modified to improve the strain. To do this, it is necessary to use genomic techniques, enabling collection of all the cellular information at a given time, i.e. the "transcriptome", which is the expression of all the genes. The approach consists in obtaining a global view of how the microorganism works, first of all, and then selecting the relevant genes to be modified.

The research conducted for this thesis focused on identifying the role of certain regulating genes of *T. reesei* in the production of cellulases. In particular, it used DNA chips to study the impact of culture conditions on the expression of some 9,000 genes of the fungus.

It was revealed that the culture conditions modified the expression of at least 600 genes, which are therefore involved in the enzyme production process. The advantage of this global approach is that it was possible to identify several genes that were not known to be involved in the production of cellulases.

Several of these genes may have an impact on the performance of strains, and the most promising ones are currently being examined in more detail with a view to industrial application.



Main categories of genes involved in cellulase production.

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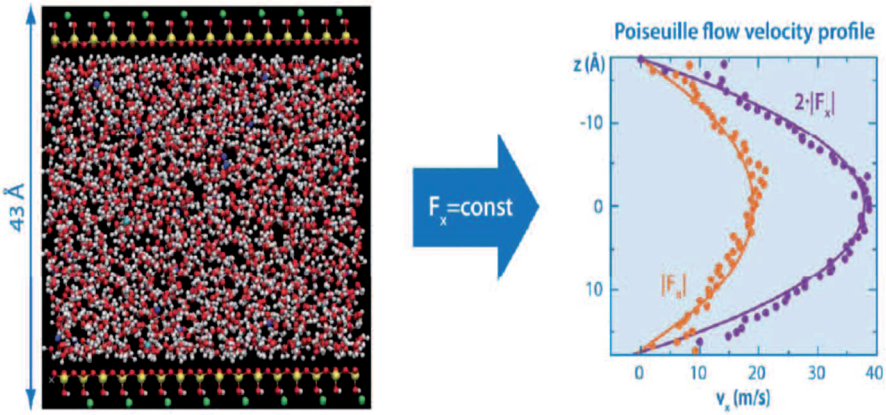
Molecular modeling of clay in contact with a CO_2 reservoir

Thesis by Alexandru Botan

Social acceptance of the geological storage of CO_2 needs keeping the integrity of the argilaceous overburdens of reservoirs. Understanding the level of impermeability requires a detailed description of transport processes in environments in which the pores have small dimensions on the order of few molecular sizes. Since liquid/solid interface effects may dominate, the emergence of some original behaviors can be expected. Thus, for solids having a surface charge (clays), swelling effects are observed, inducing hydromechanical coupling that may lead to macroscopic leakage phenomena.



Out-of-equilibrium molecular dynamics of brine + CO_2 in a clay pore. By applying a constant force to the molecules, a Poiseuille flow is obtained, from which the viscosity of the fluid can be deduced.

The research conducted as part of this thesis aimed to isolate non-trivial molecular effects in nanoporous environments — natural or otherwise — and to quantify these and estimate their impact on large-scale continuous description. Using molecular dynamics, the focus was placed on the modeling of Brine/CO_2/Clay systems, at thermodynamic equilibrium and then under forced flow conditions in a "pore" of variable size (see *Fig.*).

Using Brine/CO_2/Clay Monte-Carlo simulation codes, equilibrium states were quantified and compared with measured data. These simulations demonstrated that, in the interlayer nanopores, contact with a CO_2 reservoir did not induce any additional swelling or shrinking. In addition, it appears that montmorillonite can adsorb CO_2 in interlayer pores, a phenomenon which is currently being tested experimentally.

Furthermore, the thermodynamic properties of the H_2O/CO_2 mixture in the clay mesopores, as well as the liquid flow within nanopores with a size greater than 4 nm, have been simulated. It appears that this flow can be described using the Navier-Stokes equation, as long as the standard non-slip condition is replaced by a surface fluid sliding condition. Keeping the non-slip condition induces a significant error.

This finding allows to keep a continuous description and thus to set-up scale-change tools needed to parameterize traditional continuous descriptions that are used at the standard macroscopic scales of interest.

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S. Tazi, ***A. Botan,*** *M. Salanne, V. Marry, P. Turq, B. Rotenberg,* Diffusion and viscosity of water from molecular simulations: comparing methods and force fields, *J. Phys. Condens. Matter, 24, 284117.*

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Awards

- ***Antoine Fécant*** *was awarded the 2012 young researcher's prize by the city of Lyon, in the "Sustainable Development Sciences and Engineering" category (28 September).*
- ***Manel Fourati****, a PhD student, was awarded the best poster prize at the opening session of the 22nd International Symposium on Chemical Reaction Engineering held in Maastricht (Netherlands) from 2 to 5 September 2012.*
- ***Frank Bourdelle,*** *a PhD student, was awarded the thesis prize by the French Society of Mineralogy and Crystallography during the Serpentine days 2012 workshop held from 2 to 6 September.*

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Special issue focusing on theses

	Thesis topic	Scientific contact at IFPEN
Ibrahim Abada *2012 Yves Chauvin prize-winner*	Modeling of the natural gas markets in Europe, in oligopolistic competition, the GaMMES model and a few applications. **Article:** *A GaMMES model for the gas industry*	olivier.massol@ifpen.fr
Mickaël Barbier	Multi-scale sedimentary diagenetic and structural heterogeneities of the Madison carbonate formation (Mississippian, Wyoming, USA): reservoir implications. **Article:** *Gaining a better understanding of carbonate reservoirs*	youri.hamon@ifpen.fr
Joëlle Eyssautier	Characterizing and modeling asphaltenes in reactional hydrotreatment conditions. **Article:** *How asphaltenes aggregate*	loic.barre@ifpen.fr
Marie Savonnet *2012 Yves Chauvin prize-winner*	Synthesis of new MOF-type materials with acidic and basic properties and evaluation in catalysis. **Article:** *Functionalization of MOFs*	nicolas.bats@ifpen.fr
Thomas Portnoy	Analysis of the Trichoderma reesei transcriptome to improve cellulase production. **Article:** *Trichoderma reesei: it's all in the genes*	antoine.margeot@ifpen.fr
Alexandru Botan	Modeling transport processes in low-permeability porous environments: a molecular dynamics approach. **Article:** *Molecular modeling of clay in contact with a CO_2 reservoir*	benoit.noetinger@ifpen.fr