Science@ifpen

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*IFPEN develops and hones its scientific skills in a variety of contexts by being a versatile player in the French research and innovation system, helping to develop a European research community, providing expert advice to public bodies, industry and local authorities, leading thinking on future energy research and, lastly, by training young researchers to the very highest level in all the relevant disciplines.*

*In order to pursue this dynamic mission, IFPEN relies heavily on its Expert network, whose ranks have been swelled in early 2013 by the appointment of new expert directors and experts. Issue 13 of Science@ifpen aims to share with you the scientific contribution of these new experts by illustrating the diversity and complementarity of their skills, ranging from geoscience through to economics, not to mention soft chemistry, chemical physics and fluid mechanics. A sample of their research is offered in the form of achievements which contribute to the success IFPEN and the esteem in which it is held.*

*I hope you enjoy reading this issue.*

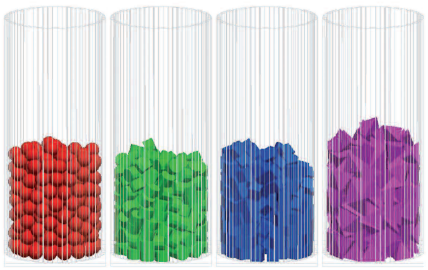
*Xavier Montagne,*
*Associate Director, Scientific Division*

# Microstructure of granular media: from sand pile to catalyst bed

Fixed bed catalytic reactors are large cylindrical containers in which a fluid (liquid, gas or a mixture) flows through a bed of static particles to produce a chemical reaction at the fluid/particle interface. A variety of coupling phenomena come into play ranging from chemical kinetics on a nanometric scale to the dynamics of the process on a metric scale. Furthermore, on an intermediary scale, i.e. at particle level, the flow dynamics is highly dependent on the microstructure of the particle bed; this microstructure depends in turn on the filling process of the reactor.

In order to understand the microstructure – flow dynamics – reaction efficiency relationship, IFPEN has been developing its own granular dynamics tools for several years based on a computational code, Grains3D, which makes it possible to simulate all of the inter-particle contacts using a Discrete Element Method. This fully parallel code provides a means of treating systems on a quasi-industrial scale composed of several tens of millions of particles. Grains3D is unique because it can handle non-spherical and angular particles. It provides access to local data at the centre of the bed including porosity, orientation of non-sphericle particles or tortuosity, and offers the opportunity to describe the microstructure in statistical terms (average value, standard deviation, etc.).

Grains3D is a generic granular media dynamics tool with a variety of applications in the energy field and beyond (rotating drums, subsidence/collapse, avalanches, etc.).



*Packing of various convex particles in a cylindrical container.*

***A. Wachs,*** *L. Girolami,* ***G. Vinay, G. Ferrer,*** Grains3D, a flexible DEM approach for particles of arbitrary convex shape - Part I: numerical model and validations, *Powder Technology, 2012, 224, 370-389. http://dx.doi.org/10.1016/j.powtec.2012.03.023 www.peligriff.com*

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# Towards improved modeling of speculative phenomena on the oil markets

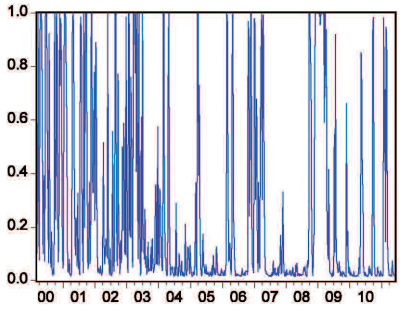
Studying oil markets involves analysing the dynamic of crude oil prices, which can experience significant fluctuations, such as those observed in the summer of 2008. Analysis of the factors determining these fluctuations involves studying the existence of speculative phenomena.

Short and long-term relationships between spot and future prices on the oil markets are estimated using econometric modeling. However, short-term dynamics, which are very unstable and characterised by periods of intense volatility, are not well handled by these models.

In order to offset these problems, a simulation based on the Markov chain change of state was therefore used. It involves considering two states for the short-term dynamic: a standard state, which corresponds to the majority of observations, and a crisis state corresponding to periods of crisis. The unconditional probability of being in the crisis state (cf. figure) is explained in a probit econometric model by the volume of delayed transactions on the financial markets for oil.

These simulations do not exclude the hypothesis of a long-term balance between spot and future prices on the oil markets. However short-term high-volatility phenomena appear which can be associated with volumes of transactions on the financial markets.

Estimation of speculative phenomena therefore involves exploring interactions and contagion phenomena:
- on the one hand, between prices on the various commodities markets,
- on the other hand, on the tranmission of crude oil prices to the price of oil products and right down to the end consumer.




*Unconditional probability of the crisis state.*

*E. Hache, F. Lantz,* Speculative trading and oil price dynamic: A study of the "WTI market", *Energy Economics, 2013, 36, 334-340.*
*DOI: 10.1016/j.eneco.2012.09.002*

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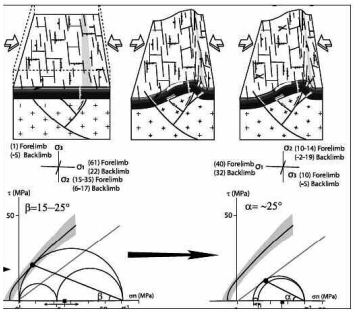
# A core sample to improve basin models

Over the last decade, oil exploration has made increasing use of basin modeling software. IFPEN is a major player in the research and development of these tools with its TemisFlow™ software. Looking beyond thermal and hydraulic calculations, simulating the mechanical evolution of basins over the course of geological periods is an important area of progress in which IFPEN is active with a view to predicting the height of trapped hydrocarbons more accurately.

In order to achieve this, knowledge of the evolution of stresses over the course of geological history is required. However, the methods available from outcrop data only provide some of the stress tensor components. Our knowledge of paleo-stresses is therefore limited, unless we can better exploit data accessible by drilling. By following this approach, in partnership with the Institut des Sciences de la Terre de Paris (ISTEP), a method has been developed allowing access to the complete tensor by using core samples from drilling.

This method involves observing twins which appear in calcite crystals which have undergone tectonic stress. These observations, carried out on several generations of crystals and combined with paleo-burial depth data, have allowed us to track the evolution of complete paleo-stresses and to estimate paleo-high pressure in real cases.

A powerful tool is now available to study the phenomena which produce natural stresses, and therefore earthquakes, and damage to reservoir caps. To be fully operational, observation of calcite twins must be automated. Promising preliminary tests have been carried out with the Institut de Chimie Moléculaire et des Matériaux d'Orsay (CMMO).




*Evolution of stresses (Mohr space, bottom) during the formation of a fold in Wyoming (top).*

*K. Amrouch, N. Beaudoin, O. Lacombe, N. Bellahsen, J.-M. Daniel,* Paleostress magnitudes in folded sedimentary rocks, *Geophys. 2011, Res. Lett., 38.*
*DOI: 10.1029/2011GL048649*

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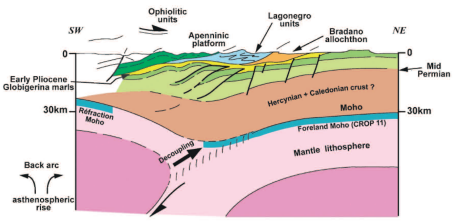
# Images worth their weight in black gold

The nature of the eastern Mediterranean crust (which is thinned and still either continental, or by contrast oceanic) is the subject of much debate as it affects the possibility of finding oil there. IFPEN has therefore carried out research to try to determine the characteristics of this basin in order to gain an understanding of how it was formed.

Imaging of the crust and tomographic images of the upper mantle have made it possible to carry out deep soundings from the surface to a depth of several hundred kilometres. These techniques have therefore recently helped to improve our understanding of the architecture of the Mediterranean Alpine chains and to reassess both the supposedly oceanic nature of the lithospheric plate now plunging under Calabria and paleographic reconstructions of the central Mediterranean.

Moreover, there are close similarities in geometry and deformation between the sedimentary series of the deep Ionian Basin (between Calabria and Libya), the Sicilian Channel (between Sicily and Tunisia) and those found in the Tellian Atlas (in northern Algeria). This means that they can all be attributed to the very thinned distal part of the former passive continental margin of Africa and not to the remains of a Mesogean ocean which was thought to have separated Africa in the south from Apulia in the north.

The continental crust in the Adriatic domain is also decoupled from its mantle lithosphere under the Apennine chain, as the base of the crust has gradually been lifted under the chain (shallow Tyrrhenian Moho), but still connects with its lateral equivalent beneath the adjacent flexural foreland basin (deeper Adriatic Moho) (cf. figure). This delamination of the crust demonstrates the subduction of the infracontinental African mantle lithosphere under the Apennines and the Calabrian arc. These new concepts have a number of implications for oil because there are grounds for believing that significant oil and gas fields can be found in the Mediterranean. The fact that the former continental margin of Africa extends offshore deep into the central Mediterranean (Ionian Basin and Libyan Sea) should encourage explorers to become interested in this part of the offshore Mediterranean too.




*F. Roure, P. Casero, B. Addoum,* Alpine inversion of the North African Margin, and delamination of its continental crust, *Tectonics, 2012, 31, TC3006. DOI: 1029/2011TC002989*

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# Additives to enhance recovery in a crude oil environment

In practice, oil production is inseparable from water production. Very stable "water in oil" emulsions form which must then be separated by physical means (gravity separators, electrocoalescers, etc.) or primarily by chemicals means (emulsion-breaking additives).

However, there is no universal chemical formulation to treat these emulsions. The effectiveness of products is actually highly dependent on the composition of crude oil, an extremely complex product. It contains molecules with emulsifying properties (such as naphthenic acids, resins or asphaltenes) which promote the formation of stable emulsions. Furthermore, the ways in which additives act on the water/oil interface are not well understood, making it difficult to optimise the separation process.

A number of research projects have been carried out by IFPEN:
- to develop techniques to characterise the morphology and stability of crude oil emulsions;
- to understand the way in which emulsion-breaking additives act by studying their structure and impact on water/oil interface properties in particular.

All of this research has facilited the development of research methodologies which can be applied directly to extremely complex, opaque and concentrated emulsions. These methodologies will prove extremely valuable, notably in relation to enhanced oil recovery (EOR), in predicting the impact of chemical additives on emulsion separation.


***Emulsion of oil before and after separation (left) and an optical microscopic view of an emulsion (right).***

*A. Forny-Le Follotec, O. Glatter,* ***L. Barré, I. Pezron, C. Noïk, C. Dalmazzone,*** *L. Metlas-Komunjer,* Characterization of Micelles of Small triblock Copolymers by Small Angle Scattering, *Macromolecules, 2012, 45, 2874-2881. DOI: 10.1021/ma202610n*

***C. Dalmazzone, C. Noïk, J.F. Argillier,*** Impact of Chemical EOR on the Separation of Diluted Heavy oil Emulsions, *Energy & Fuels, 2012, 26 (6), 3462-3469. DOI: 10.1021/ef300083z*

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# Soft chemistry in the world of crude oil

Today, most industrial methods for preparing heterogeneous catalysts are based on the reactivity of an oxidic surface with a hydrosoluble mineral or, more seldom, organic, precursor. However these methods do not allow accessing to many promising chemico-physical properties. These original combinations (e.g. dispersion of large number of small active phase particles on low surface area carriers) could however lead to significant improvements in terms of selectivity, or to realise some "dream" reactions (e.g. direct conversion of $CH_4$ into alcohol or higher hydrocarbons). Among the different routes which may bring breakthroughs, the "chimie douce" approach is currently studied at IFPEN to synthesise encapsulated or "core-shell" nanoparticles. This large research field which provides access to nanoparticles with new properties in terms of morphology and structures is constantly evolving, due, for example, to the combination of new reagents with specific chemical properties (ionic liquids, block copolymers, dendrimers) and original physico-chemical processes (micro-emulsion, supercritical conditions, autoassembly assisted by tensioactives).

It is possible, for example, to obtain quasi-spherical particles of $MoS_2$ coating a ZnS core (figure 1)[1]. These particles, which are characterised by their "fullerene like" morphology of curved and continuous layers of $MoS_2$ slabs, have demonstrated remarkable properties in hydrotreating reactions and photocatalysis.

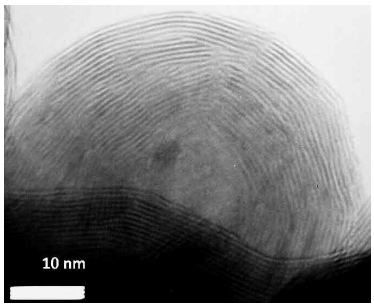


*Fig 1. Nanoparticle of $MoS_2$@ZnS obtained by glycothermal synthesis of ammonium heptamolybdate.*

Another example of a solid obtained using "chimie douce" approach consists of Pd nanocubes exposing the crystallographic [100] plane, and coated with a thin mesoporous silica layer (figure 2)[2].

The materials science is currently experiencing spectacular developments

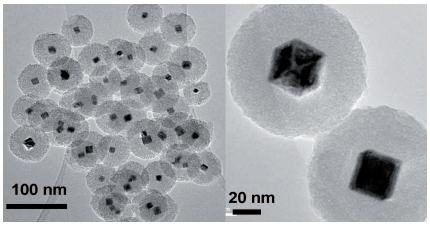


*Fig 2. Nanoparticles of Pd coated in mesoporous silica (C. Boissière, C. Sanchez, LCMC Paris, A. Chaumonnot, IFPEN).*

and is an area of first importance for innovation in order to improve and develop new processes to meet energy and environmental challenges.

*(1) A. Nogueira, R. Znaiguia, **D. Uzio,** P. Afanasiev, G. Berhault, Applied Catalysis A: General, 2012, 429-430, 92-105.*

*(2) N. Batail, **I. Clémençon, Ch. Legens, A. Chaumonnot, D. Uzio,** Eur. J. Inorg. Chem., 2013, 1258–1264.*

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## IFPEN/Inra bioeconomics framework agreement

*IFPEN has recently signed a five-year framework agreement for scientific and technological research collaboration in bioeconomics. The aim is to develop thinking on the challenges associated with introducing renewable carbon into the energy field and to draw up a joint research and innovation strategy.*

## Awards

• **Thomas Dutriez,** *a former IFPEN PhD student has been awarded the Phillips Prize at the 10th symposium on chromatography in the multidimensional gas phase (GC-2D) for his research at IFPEN on this subject (12 to 16 May 2013).*

• **Jean-Baptiste May-Carle,** *a former IFPEN PhD student has won third prize for the "young researcher" poster at the 10th CONCAWE conference for his research at IFPEN on the use of ethanol in diesel engines (25 and 26 February 2013).*

## HDR

• ***André Nicolle,*** *HDR at Orléans University: "Kinetic modelling of nitrogen oxide in industrial processes" (5 July).*

## Upcoming scientific events

• *IFP Energies nouvelles "Rencontres scientifiques" event* ***– Viscoplastic Fluids: From Theory to Application –*** *18-21 November 2013, IFPEN Rueil-Malmaison.*

• *IFP Energies nouvelles "Rencontres scientifiques" event* ***– Creating the next generation laboratory to develop innovative materials and additives for energy (NEXTLAB 2014) –*** *2-4 April 2014, IFPEN Rueil-Malmaison.*

• *IFP Energies nouvelles "Rencontres scientifiques" event* ***– Photocatalysis for Energy –*** *15-17 October 2014, IFPEN Lyon.*

## Publications

• *Fabrice Bertoncini, Marion Courtiade-Tholance, Didier Thiébaut –* ***"Gas Chromatography and 2D-Gas Chromatography for Petroleum Industry – The Race for Selectivity"*** *– Éditions Technip. ISBN: 9782710809920*

• *Hervé Toulhoat, Pascal Raybaud –* ***"Catalysis by Transition Metal Sulfides – From Molecular Theory to Industrial Application"*** *– Éditions Technip. ISBN: 9782710809913*

• *François Badin –* ***"Hybrid vehicles – From components to system"*** *– Éditions Technip. ISBN: 9782710809944*

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