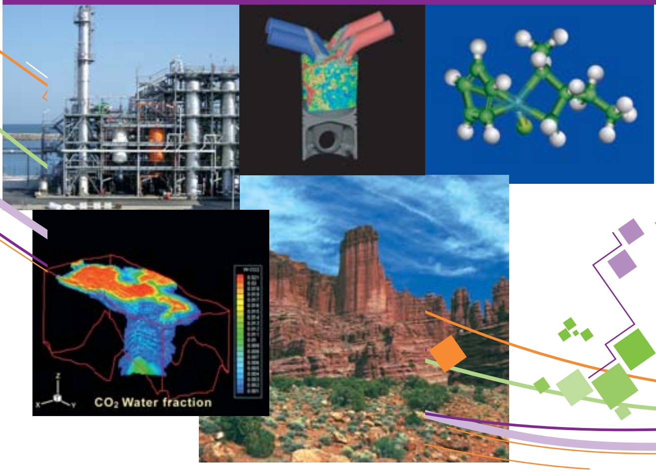


Science@ifp
No 3 - February 2008

Observing in 3D on nanometer scale

A few readers have expressed their surprise that some of the scientific articles referred to in Science@ifp date from before 2000. It is not Science@ifp's intention to mention only recent contributions. Work with major impact have a place in this letter.

Now, it takes several years for this impact to emerge, whence the choice of less recent references. For example, in this issue, number 3, one of the articles referred to on ionic liquids has been mentioned more than 450 times in the literature. And one of the articles on molecular modeling referenced in issue number 2 has been mentioned more than 90 times*.*

I hope you enjoy reading this issue!

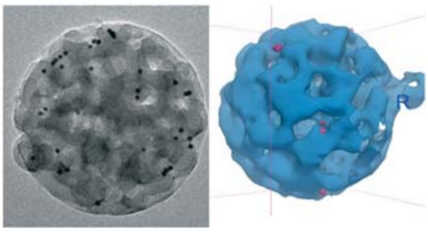
Philippe Ungerer
Scientific Director

** source: ISI Web of Knowledge*

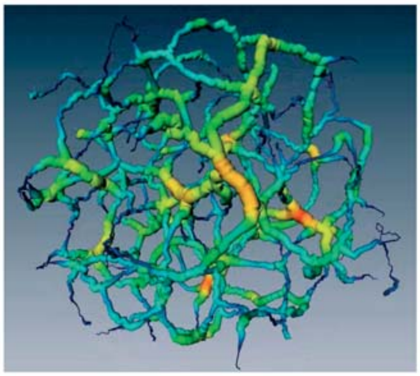
Electron tomography, or 3D MET, combines the capabilities of conventional transmission electron microscopy, which can be used to observe nanometric objects, with those of X-ray tomography, commonly used in medicine, which allows the reconstruction of an object in 3D. The technique is based on the acquisition of images of the object from different points of view, followed by a virtual reconstruction.

Thanks to the development of powerful computing tools and the joint work of multi-disciplinary teams (mathematicians, computer scientists, analysts, geologists), IFP now has an effective tool that can, for example, yield a better description of the porous structure of catalysts. 3D MET makes it literally possible to navigate inside a grain of catalyst, to extract relevant quantitative information about its porosity, and to observe the locations and morphology of the metallic clusters that promote activity.

This work, done in close collaboration with the Institut de physique et chimie des matières of Strasbourg (IPCMS), makes us the French pioneers in the 3D observation of solids.



View of a spherical particle of a mesoporous aluminosilicate, approximately 250 nm in diameter, by conventional microscopy, together with its reconstruction in 3D.



Representation of the porosity of the same particle, with a color code corresponding to the pore diameter (minimum diameter = 10 nm, in blue), making it possible to know the volume and connectivity of the pores. This in turn enables to model the diffusion of substances within the particle of catalyst.

*Ersen O., Hirlimann C., Drillon M., Werckmann J., **Tihay F.**, Pham-Huu C., Crucifix C., Schultz P., Solid State Sci. 9, 2007, 1088-1098.*

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IFP is a world-class public-sector research and training center, aimed at developing the technologies and materials of the future in the fields of energy, transport and the environment.

Innovation Energy Environment

Scaling up flows in heterogeneous porous medium

Reservoir rocks are porous media that are extremely heterogeneous over an extensive range of scales — from the micron to the kilometer. Similar features are observed in catalysts — from the nanometer to the millimeter. The laboratory tools and geoscience techniques used to characterize these porous media now yield representations that are highly realistic and also probabilistic because an exhaustive description is impossible. In order to get an accurate large scale description of mass and heat transfers, the details of the local transport processes must first be scaled. Use is made of a vast array of techniques: homogenization in mathematics, averaging in mechanics, coarse graining in physics, etc.

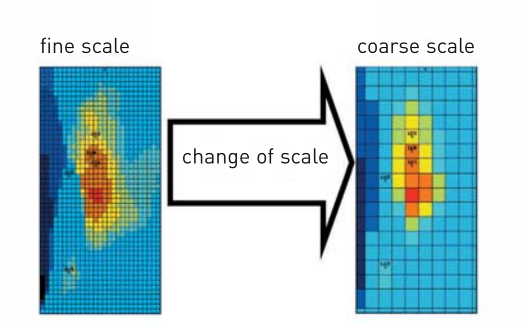

Fig. 1

For example, to develop petroleum reservoirs, we model flows (numerical solutions of partial differential equations) in 3D geological structures described by tens of millions of fine meshes. The limitations of computers then require us to reduce the number of meshes by one or two orders of magnitude, by a proper aggregation of fine meshes accounting for the fine scale mass transfer processes *(Fig. 1)*.

Using techniques derived from renormalization theory, we have generalized the effective permeability formula to the anisotropic case via a single coefficient ω given by the master curve of figure 2.

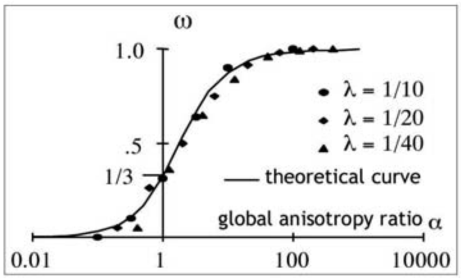

Fig. 2: Variation of coefficient ω as a function of geological anisotropies.

This coefficient depends on the anisotropy of geometry (λ) and of fluid transfer (k_v/k_h). The analytical results are perfectly in line with the numerical results from a project with Total. These results are now being generalized to other types of media and to other transport processes.

Nœtinger B., *Transport in porous media, 15, 99-127, 1994.*
Nœtinger B., Artus V., *Zargar G., Hydrogeol J. , 13, 184-201, 2005.*

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Viscosity of fuels by molecular dynamics

The new generation of low-consumption flexfuel engines must be able to operate with different types of diesel/biodiesel mixtures. This calls for knowledge of the thermophysical properties of these mixtures, in particular their viscosities, under extreme injection pressure conditions (around 2,500 bars). But obtaining these data from conventional correlative models is possible only with known compositions and at relatively low pressures (less than 1,000 bars). In addition, the high pressure makes the experiments expensive, even difficult to perform.

Accordingly, to determine the viscosities of various fuels under extreme conditions, IFP, working with the University of Orsay, uses molecular dynamic simulation. This is now possible thanks to modern analysis techniques, such as 2D chromatography, which yield good descriptions of the compositions. For the simulation of fuels, the excessively large number of real components, more than 250, must be reduced to a few groups. The grouping is done by families and physical properties (lumping). The viscosities of diesel/biodiesel mixtures under extreme injection conditions can then be estimated.

Nieto-Draghi C., Ungerer P., *Rousseau B., J. Chemical Physics 125 (4), Article number: 044517, 2006.*
Nieto-Draghi C., Bonnaud P., Ungerer P., *J. Physical Chemistry C 111, 15942-15951, 2007.*

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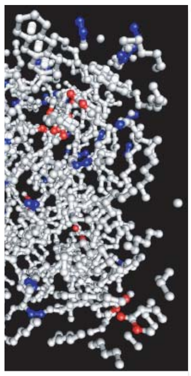

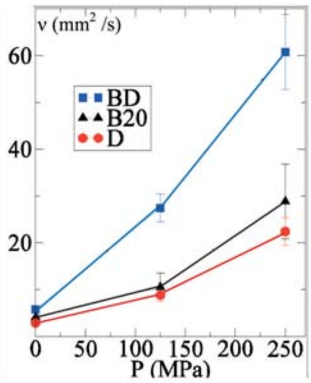

Left: simulation box illustrating the B20 mixture (standard diesel + 20% biodiesel) under normal conditions (C = grey; O = red; double bonds or "insaturations" = blue).

Right: determination by simulation of the kinematic viscosity as a function of pressure at 313 K. Petroleum diesel (D), B20 mixture, and pure biodiesel (BD).

The biodiesel studied is a methyl ester of colza oils.

Ionic liquids for the environment

IFP's major expertise in homogeneous catalysis has led to the industrial development of oligomerization processes such as Dimersol and Alphabutol. In order to make these processes cleaner, IFP has since developed two-phase liquid-liquid catalysis in ionic liquids.

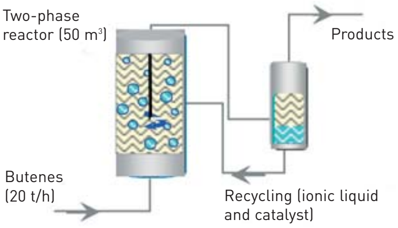

Fig. 1: Dimerization of butenes in a two-phase medium to reduce discharges.

These media, which consist only of non-volatile ions and have physico-chemical properties that can be modulated, have been used as solvents to immobilize and recycle homogeneous catalysts.

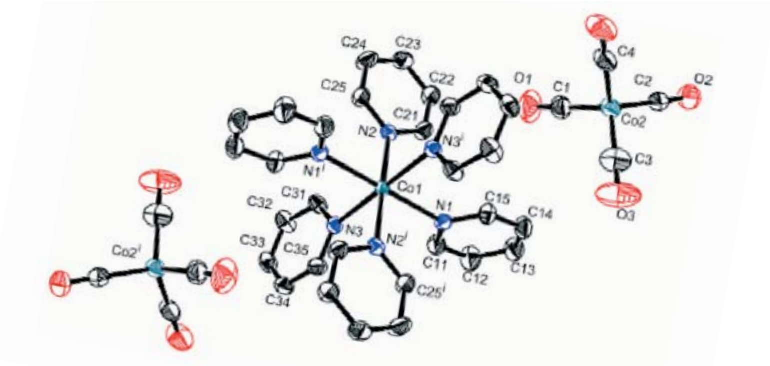

Fig. 2: Structure (X-ray diffraction on monocrystals) of the ionic complex $[Co(pyridine)_6]^{2+}[Co(CO)_4]^{2-}$ - immobilized in the ionic liquid; it generates the active species $[HCo(CO)_4]$ under CO/H_2 pressure.

By using chemistry and engineering expertise, the new two-phase Difasol process, which combines reaction and separation, has made it possible to limit waste while improving the yield of desirable products and reducing the reactors' volume *(Fig. 1)*.

Ionic liquids have also recently served as the basis for a simple and original recycling concept for cobalt-based catalysts used in the hydroformylation of olefins *(Fig. 2)*.

Today, ionic liquids are booming: they are used as solvents in separation and purification processes, as electrolytes in batteries, and for the synthesis of new materials. They are marketed in particular by a French SME (Solvionic).

Chauvin Y., Olivier H., *Chemtech, 26-30, 1995.*
Magna L., Harry S., Proriol D., Saussine L., Olivier-Bourbigou H., *Oil & Gas science and technology, 62, 6, 775-780, 2007.*

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Advanced fuels for HCCI combustion

When it comes to controlling greenhouse gas emissions, which means controlling fuel consumption, the greater efficiency of the diesel engine makes it the preferred solution. However, the drastic reductions of NOx and particulates emissions required by the Euro 5 and Euro 6 regulations are a real challenge.

To meet these ambitious objectives, low-temperature combustion such as HCCI combustion (Homogeneous Charge Compression Ignition), by dividing NOx and particulates emissions by a factor of 10 to 100 in the raw exhaust gas, is a promising alternative to cumbersome and expensive depollution systems.

However, this approach is today feasible only in a limited part of the desired operating range.

IFP, through work done in collaboration with the laboratory (Icare-Orléans) and on engine test benches, has shown that a suitable fuel formulation can significantly extend this range. The work done on model mixtures has for example revealed the impact of an acetal on the initiation and development phases of combustion: methylal makes it possible to decrease the intensity of the cold flame (control of the inflammation time) while increasing the rate at which energy is given off during the hot flame, thereby optimizing combustion timing. This model work on acetals holds promise of better control of HCCI combustion by incorporating acetal molecules, or other, less toxic, molecules, in the fuel.

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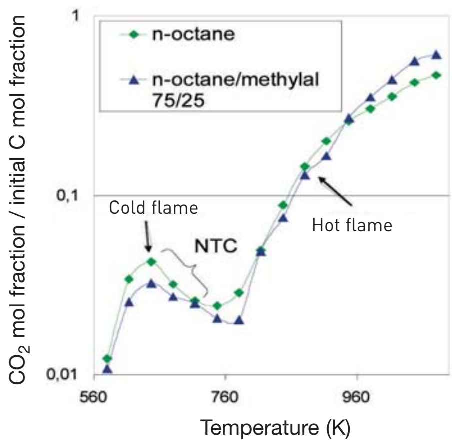

The addition of 25% methylal (triangles) controls the activity of the cold flame, allowing better control of the global combustion while delivering a more energetic hot flame.

Alseda D., Montagne X., *Dagaut P., 8th International conference on engines for automobile, SAE Naples Section, 16-20 september 2007.*

Large-scale distribution of durable goods and energy demand

The pace at which energy demand has grown since the beginning of the 2000s has surprised most forecasters. A "standard" statistical model (i.e. one assuming linear relations) of the interactions between standard of living and energy consumption cannot make sense of the phenomenon observed.

IFP has accordingly undertaken to develop a regional and sectorial model of energy demand encompassing the process of durable goods being distributed on a large scale in a population, which results in the nonlinearity in the relation between per capita income and individual energy consumption.

The practical application of this theory led to a regional model (99 countries and 2 regions) of demand for vehicles and for motor fuels *(Fig.)*. Our model explains the recent faster growth in energy demand, and shows in addition that the price rise observed since 2002 was necessary in order to contain demand and keep its growth in phase with oil supply development.

This theory could be applied to energy demand in other sectors, for example the residential sector.

Lescaroux F., Rech O., The Energy journal, 29 (1), pp. 41-60, 2008.

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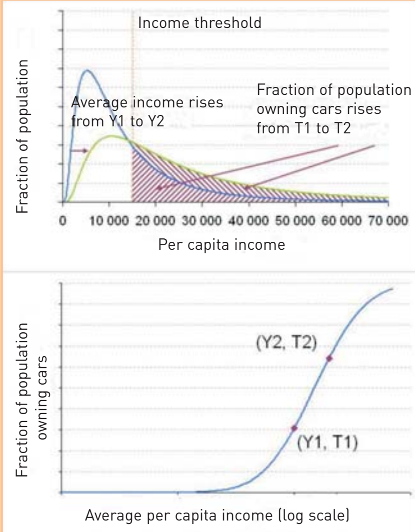

To simplify: a consumer in a given country decides to acquire a durable good that consumes energy (car, electrical appliance, etc.) when his/her revenue exceeds some threshold (Ys), which varies over time and from one region to another depending on sociological, geographical and tax parameters. Assuming that income distribution in a population follows a log-normal law, the fraction of the population owning the durable good in question is represented by the hatch-marked zones. It is 1/2 when the median income is Ys. The rising standard of living then leads to a sigmoid (S-shaped) distribution of the durable good, resulting in a sigmoid change of per capita energy consumption.

Honors

• **Jonathan Chauvin** *was awarded on 11 December 2007 the ParisTech thesis prize for his thesis, "Estimation et contrôle d'un moteur diesel HCCI" (Estimation and control of an HCCI diesel engine).*

• *The Journal of petroleum science and engineering has devoted a special issue to* **Alain-Yves Huc**, *geochemist at IFP (volume 58, Nos. 3-4, 2007).*

• **Alireza Tehrani** *was awarded by the Association des économistes de l'énergie (French association for energy economics), on 6 December 2007, second prize for the best article by a doctoral student in energy economics in France, for the paper entitled "Allocation of CO_2 emissions in petroleum refineries to petroleum joint products: a linear programming model for practical application".*

Books

Bernard Zinszner and François-Marie Pellerin (Total): A Geoscientist's guide to petrophysics, Éditions Technip.

Accreditation as director of research (HDR)

• **Anne Jaecker**
HDR, University Louis Pasteur, Strasbourg: Les polluants et la pollution atmosphérique : de la modélisation à l'expérimentation (Pollutants and atmospheric pollution: from modeling to experiment) (20/12/07).

• **Christophe Pichon**
HDR, University Claude Bernard - Lyon I: Structure étendue et structure locale des solides dans le domaine du raffinage et de la pétrochimie : apport des grands instruments analytiques (Extended structure and local structure of solids in the field of refining and petrochemicals: contribution of large analytical instruments) (19/12/07).

• **Emmanuel Fontaine**
HDR, University of Nantes, on the theme: Problèmes d'interactions fluide-structure en hydrodynamique navale et offshore (Problems of fluid-structure interactions in naval and offshore hydrodynamics) (07/12/07).

Newcomer at IFP

• **François Badin** holds an HDR in Environmental engineering from the University of Savoie (1999). In 2007, he was a member of the International energy agency's group of experts on hybrid vehicles. He works as an expert with the Predit 3 program and is a member of the Scientific and technological board of the Mobility and advanced transports competitiveness cluster.

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