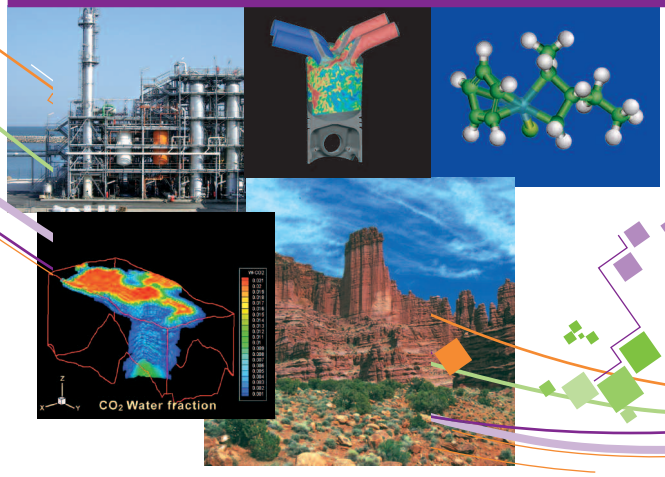


Science@ifp
No. 6 - January 2010

Simulation and experimentation are two interconnected activities which are central to the research work carried out at IFP. The development of tools for simulation and modeling purposes – the results of which are subsequently compared with experimental data – makes it possible to represent and gain a better understanding of complex mechanisms, to reduce development times and to predict behavior.

This approach has proved successful in many of IFP's research fields (combustion, catalysis, CO_2 storage, etc.), as demonstrated by the scientific results presented by our researchers in this issue. What's more, two of them are winners of the Yves Chauvin thesis prize, awarded each year to IFP's best PhD student.

Their research work, together with that of their colleagues, opens up new opportunities for innovation in the key fields of energy, transport and the environment.

Philippe Ungerer
Scientific Director

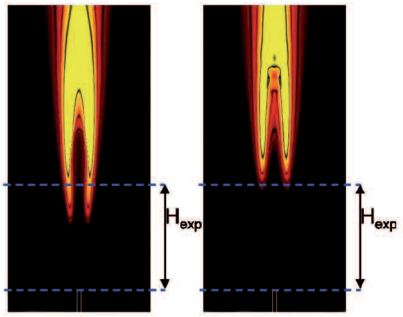
Combustion is laying the table!

Numerical simulation is often used for the development of internal combustion engines. Turbulent combustion modeling, for example, makes it possible to predict pollutants and heat release. It requires an accurate representation of the chemistry of heavy hydrocarbons. In turn, this involves highly complex kinetic schemes with hundreds of species. However these schemes cannot be used directly in computational fluid dynamics (CFD) codes for reasons associated with the calculation time.

Tabulated chemistry provides a solution to this problem. The objective is to use tables to store chemical quantities as functions of a small number of variables that are then transported into the CFD code.

The ADF-PCM *(Approximated Diffusion Flames – Presumed Conditional Moment)* model recently developed at IFP is based on a dual chemical tabulation. The first table is generated using homogeneous reactors with detailed chemistry. Diffusion effects are then introduced by calculating the approximated diffusion flames. Finally, the second table is generated using probability density functions to apply the model to turbulent configurations. These different stages imply that the calculation times associated with this model are extremely short.

The ADF-PCM model has been successfully validated by comparison with various experimental measurements – auto-ignition times, chemical composition and flame structure. Among other things, it could be used to predict nitrogen oxides by coupling with a specific NOx model.



Mass fraction of OH for two ADF-PCM formulations. Blue line: experimental flame lift-off height (Cabra experiment, Sandia laboratory).

J-B. Michel, O. Colin, *D. Veynante, Modeling ignition and chemical structure of partially premixed turbulent flames using tabulated chemistry, Combustion and Flame, Volume: 152, Issue: 1-2, Pages: 80-99 (Janvier 2008), DOI:10.1016/j.combusflame.2007.09.0001*

J-B. Michel, O. Colin, C. Angelberger, *D. Veynante, Using the tabulated diffusion flamelet model ADF-PCM to simulate a lifted methane-air jet flame, Combustion and Flame, Volume: 156, Issue: 7, Pages: 1318-1331 (Juillet 2009), DOI: 10.1016/j.combustflame.2008.12.012*

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Innovation Energy Environment

Modelica, towards a standard for 0D/1D simulation?

The development of hybrid vehicles and the design of refining processes depend on the modeling of complex multi-physical systems, combining continuous and discrete problems.

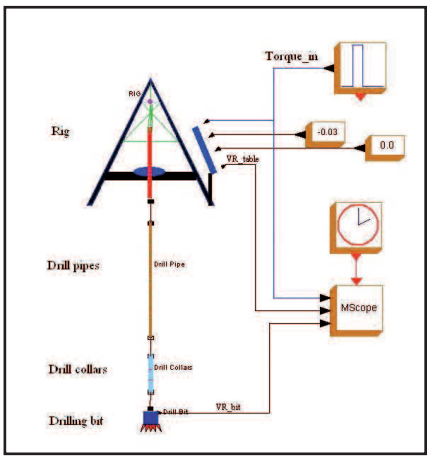
Commonly used software solutions are based on a causal representation known as system-based modeling whereby inputs and outputs are explicitly defined. The associated development time of such solutions is significant.

It is for this reason that IFP has been involved in the development of a new open-source language called Modelica, initially designed by the PELAB laboratory at Linköping University in Sweden. Using the language, a formal, acausal, implicit and modular representation can be achieved. This is known as component-based modeling. Blocks are represented by mathematical equations, the ports are implicit, without outputs or inputs, and the connectors are without directional flow.

The formal writing of mathematical equations makes the content more concise and legible and offers new functionalities such as the inversion and initialization of dynamic systems. Moreover, the runtime is reduced thanks to the generation of the analytical gradient and the integration of hybrid implicit systems by high-performance solvers.

Finally, the platform-independent language enables the use of optimization tools, interoperability and code generation, which are crucial for systems engineering.

Today, Modelica appears to be establishing itself as a standard for 0D/1D simulation. It is integrated into commercial environments (AMESim, Dymola, etc.) as well as open environments (OpenModelica, ScicosLab, etc.). Various French and European collaborative projects involving IFP are developing it further.



This drilling system model is represented in Modelica/ScicosLab using nine implicit blocks. An explicit representation would have required more than 500 blocks.

Z. Benjelloun-Dabaghi, N. Najafi, A New Modelica Model and Scicos Simulation for 0D/1D Nonlinear Complex Systems. Oil & Gas Science and Technology - Rev. IFP 63 6 (2008) 723-736, DOI:10.2516/ogst:2008042

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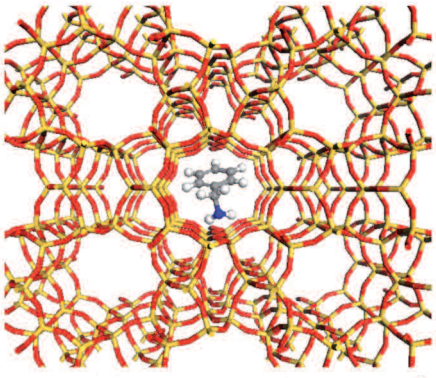
Zeolites on demand?



Modeling of an organic structure-directing agent in the pore network of zeolite materials.

Zeolites are widely used in the refining and petrochemical industries, due to their acidity and their microporous network that lends itself to the conduct of highly selective reactions. Each zeolite has a specific porosity and hence is associated with specific catalysis properties. The discovery of new structures is therefore crucial.

With a view to rationalizing this research, molecular modeling and high through put experimentation (HTE) techniques have been used in tandem.

Zeolite synthesis involves the use of structure-directing agents that must be carefully selected. Hence the development of a new methodology for selecting structure-directing species. The methodology involves the calculation of energy criteria and therefore makes it possible to eliminate organic species that are not conducive to orientation of the crystallization of the target material. The organic species selected are then tested for a range of precursor gel compositions, via the use of an HTE tool. This research has led to the discovery of new zeolite phases, particularly IZM-2[1] and STA-14[2].

The prospective applications for this research are numerous, particularly in terms of the identification of cheaper structure-directing species for materials that are known and already used in catalysis, or the synthesis of zeolites with hypothetical structures. Zeolites with the desired catalytic properties could then be designed on demand.

(1) A. Fécant, N. Bats, FR 2 918 050 (2009)

(2) M. Castro, Raquel Garcia, Stewart J. Warrender, Z. Slawin, Paul A. Wright, Paul A. Cox, A. Fecant, C. Mellot-Draznieks and N. Bats, Co-templating and modelling in the rational synthesis of zeolitic solids, Chemical Communications, Issue: 33, Pages: 3470-3472 (2007), DOI: 10.1039/b705377k

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Pseudo-Bridging Silanols revealed

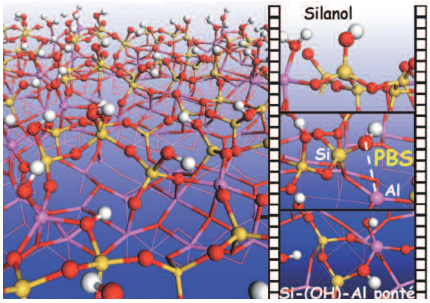
Amorphous silica-aluminas (SiO2-Al2O3) are used as heterogeneous catalyst supports in fine chemistry, petrochemistry and refining, including in biomass conversion. Owing to the amorphous character of silica-aluminas, an accurate understanding of the exact nature of the acid sites present at the surface is crucial for optimization of catalytic properties.

Quantum calculations coupled with force field dynamics have been used to propose atomic-scale representation of the surface of this catalyst. On the reference gamma-alumina model (γ-Al_2O_3)[1], the interaction of silica derivatives (SiO_2) has been modeled in an original manner, by exchange with surface hydroxyls and adsorption of a silica film[2].

Molecular dynamic simulations reveal the formation of a surface mixed amorphous alumino-silicate phase at high temperatures. Moreover, quantum modeling of water adsorption on this same surface has demonstrated the existence of new types of Brønsted acid sites. These sites dubbed "Pseudo-Bridging Silanols" (PBS), may explain the specific chemical behavior of amorphous silica-aluminas in comparison with their crystallized zeolithic counterparts.

Finally, comparison of experimental and calculated spectroscopic characteristics (infrared, nuclear magnetic resonance) has led to assignment of experimental spectra.

Current research is focusing on catalytic reactivity modeling of the PBS acid sites revealed.



Model of a silica-alumina surface and sites revealed by molecular modeling. "Pseudo-Bridging Silanols" (PBS) are a source of original acid properties.

(1) ***M. Digne,*** *P. Sautet,* ***P. Raybaud, P. Euzen, H. Toulhoat,*** *Use of DFT to achieve a rational understanding of acid-basic properties of gamma-alumina surfaces, J. Catal. 226 (2004) 54, DOI: 10.1016/j.jcat.2004.04.020*

(2) ***C. Chizallet, P. Raybaud,*** *Pseudo-Bridging Silanols as Versatile Bronsted Acid Sites of Amorphous Aluminosilicate Surfaces, Angew. Chem. Int. Ed. 48 (2009) 2891, DOI: 10.1002/anie.200804580*

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Improving CO_2 storage using molecular simulation

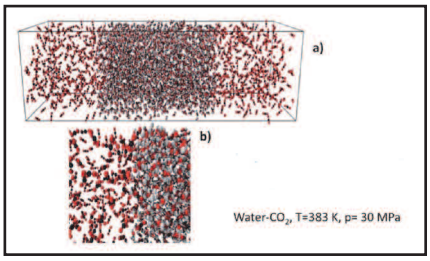
In order to ensure that the underground storage of CO_2 is secure, it is first of all necessary to confirm the confinement capacity of the cap rock on top of the reservoir. This cap rock is a low permeability, usually clayey, porous media saturated with salted water. The CO_2-rich phase can nevertheless leak out if the pressure inside the reservoir becomes too high. This risk of capillary breakthrough depends primarily on interactions between CO_2, water and rock and, especially, on the CO_2-water interfacial tension.

Working in partnership with university laboratories, IFP has been developing molecular simulation methods for a number of years now. The main applications of these methods involve the study of homogeneous systems, but also, more rarely, heterogeneous systems, for which new methodological developments are necessary.

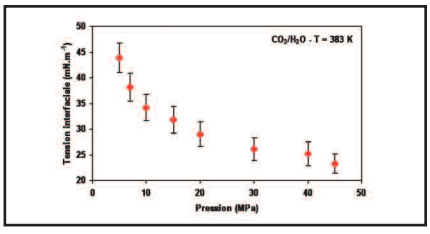
Recent research conducted in partnership with the Clermont-Ferrand Thermodynamics and Molecular Interactions laboratory has therefore focused on extending Monte Carlo simulation methods to the case of systems presenting an interface between an aqueous phase and a gaseous phase. These developments have made predictive calculation of the CO_2-water interfacial tension possible, in pressure and temperature conditions similar to those encountered in underground reservoirs.

F. Biscay, *A. Ghoufi, F. Goujon,* ***V. Lachet,*** *P. Malfreyt, Calculation of the surface tension from Monte Carlo simulations: Does the model impact on the finite-size effects?, Journal of Chemical Physics, 130, 184710 (2009) DOI: 10.1063/1.3132708*

F. Biscay, *A. Ghoufi,* ***V. Lachet,*** *P. Malfreyt, Monte Carlo simulations of the pressure dependence of the water-acid gas interfacial tensions, Journal of Physical Chemistry B, 113, 14277 (2009) DOI: 10.1021/jp906953a*



a) Simulation box illustrating the balance between an aqueous phase (in the center) and the supercritical CO_2 (on the sides) at 383 K and 30 MPa.
b) Close-up of one of the interface zones.



Interfacial tensions of the CO_2-water mixture calculated by Monte Carlo simulation.

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Using noble gases to trace CO_2

Oil exploration and geological CO_2 storage demand an in-depth knowledge of the origin of the fluids present and their migration pathways. The former involves predicting the presence and distribution of non-hydrocarbon gases (CO_2, N_2) in oil fields and the latter, tracing the CO_2 injected on a scale of several hundreds of years. Other challenges, such as enhanced oil and gas recovery, also require accurate tracing of migration processes and fluid exchanges.

Noble gases (He, Ne, Ar, Kr, Xe), present in trace quantities in all fluids, are ideal tracers for the physical phenomena involved in transport mechanisms. Their element and isotope distribution in the earth's natural reservoirs (mantle, crust, hydrosphere) also make them the most discriminating tracers for the fluids stored therein (hydrocarbons, CO_2, etc.). It is for these reasons that IFP is using noble gases for the purposes of oil exploration and CO_2 storage site monitoring.

In the latter case, on-site comparison of the concentrations of various noble gases with CO_2 concentrations enables determination of CO_2 leak percentages. Using this method, it is possible to detect leakage of less than 0.1% of the CO_2 stored by analyzing noble gases having migrated through the cap rock into a control aquifer. These methods using noble gases can also be applied to other leak scenarios, as well as to mass balance assessment of the CO_2 stored. Finally, IFP focuses on the integration of noble gases in greenhouse gas and hydrogen storage reservoir models.

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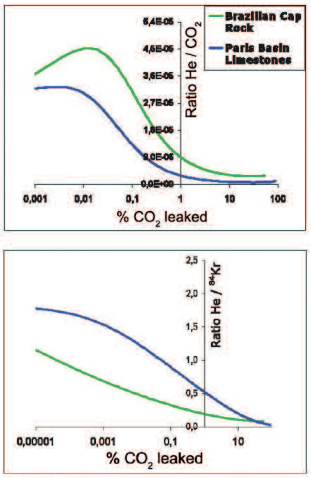

Ratio between the percentage of CO_2 leaked and the change in He/CO_2 element ratios and He/84Kr ratios in gas once it has migrated through the rock.

A. Prinzhofer, A. Battani (2003), Gas isotope tracing: an important tool for hydrocarbon exploration. Revue de l'IFP, Special Publication for B. Tissot's Jubilee, June 2003. Oil and Gas Science and Technology. Rev. IFP, vol. 58, No. 2, p.299-311, DOI: 12.2516/ogst:2003018

A. Prinzhofer, E. Vaz dos Santos Neto, A. Battani (accepted for Marine and Petroleum Geology), Coupled use of stable isotopes and noble gas signatures in accumulations of petroleum in the Potiguar Basin (Brazil)

National accreditations to supervise research (HDR)

• **Pascal Raybaud,** *IFP expert, HDR, École normale supérieure de Lyon: "From ab initio molecular modeling of surfaces to general concepts applied to heterogeneous catalysis" (28 April 2009).*

• **Olivier Colin,** *HDR, Institut National Polytechnique de Toulouse: "Three-dimensional modeling of combustion in piston engines and turbomachines" (28 September 2009).*

Upcoming scientific events

• ***Les rencontres scientifiques de l'IFP :***
1st International Conference on Chemical Looping. An Alternative Concept for Efficient and Clean Use of Fossil Resources
17-19 March 2010, IFP-Lyon
Organizational contact: frederique.leandri@ifp.fr
Scientific contact: thierry.gauthier@ifp.fr

• **9th Novel Gas Conversion Symposium**
30 May – 3 June 2010, Lyon
Contact: ngcs9@ngcb.org

Awards

• **2009 Yves Chauvin prize:** *IFP's thesis prize was awarded to Jean-Baptiste Michel for his research entitled: "Modeling of heterogeneous mixture turbulent combustion in self-ignition mode with a view to application in diesel engine simulation".*

• **Deana Soogund,** *PhD student, won the "ACS Student Award" for her paper entitled "New starting materials for highly active molybdenum-vanadium based catalysts for the hydrotreatment of residues".*

• **Sandra Buret,** *PhD student, was the winner of the "Young Professional Paper Contest" at the 2009 SPE Formation Damage conference for her paper entitled: "Water Quality and Well Injectivity: Do Residual Stable Oil in Water Emulsions matter?". The co-authors of the paper are* ***Lahcen Nabzar****, IFP Expert, and Amane Jada from the* Institut de Sciences des Matériaux *(Institute of Material Sciences) in Mulhouse.*

• **Sébastien Rohais** *was awarded the GDF Suez Yvonne Gubler thesis prize at the 12th edition of the French Sedimentologists Association's Congress held in October 2009 for his thesis entitled "Stratigraphic architecture and sedimentary flows on the southern margin of the Gulf of Corinth (Greece): field analysis, experimental and digital modeling" defended in 2007.*

Appointment

• **O. Appert** *has been appointed Chairman of the coordinating committee of the Alliance Nationale de Coordination de la Recherche pour l'Energie (ANCRE – National Alliance for Energy Research Coordination), officially launched on 18 September 2009 under the aegis and in the presence of Valérie Pécresse, French Minister for Higher Education and Research, and Chantal Jouanno, Secretary of State for Ecology.*

Book

"Corrosion et dégradation des matériaux métalliques. Compréhension des phénomènes et applications dans l'industrie pétrolière et des procédés" ***(Corrosion and degradation of metal materials. Understanding the phenomena and applications in the oil and processes industry)***
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