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Identifying interactions within complex systems in order to describe phenomena and understand reaction mechanisms so that they can be more selective: these are the objectives of IFPEN's Applied Chemistry and Physical Chemistry Division. The understanding and tools thus developed are essential in order to help forward the R&D projects in many fields, ranging from transport and traditional refining to bioprocesses and upstream production and exploration. The key to success is found in a multiscale approach that is applied both in modeling and experimentation.

Our researcher's expertise in the fields of thermodynamics, physical chemistry of complex fluids, biotechnology, electrochemistry and materials is widely recognized both nationally and internationally. They make a significant contribution to firmly establish IFPEN's scientific position, with around 45 publications per year in high-impact journals. The number of publications and citations is among the best in each of their fields: molecular modeling, oil emulsions, electrochemistry of CO_2 and fungal cellulases. The examples that follow illustrate the scientific quality of the research.

We hope that you enjoy this issue,

Véronique Ruffier-Meray
Director of the Applied Chemistry and Physical Chemistry Division

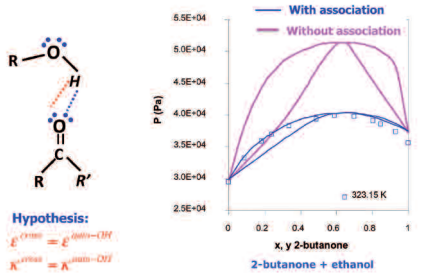
Oxygen in equations

In 1910, J.D. van der Waals was awarded the Nobel prize in Physics for his equation describing the state of liquids and gases. This "equation of state", very widely used in the oil industry, loses a significant proportion of its predictive capacity, however, when applied to fluids containing oxygenated substances.

This is because the presence of oxygenated molecules profoundly modifies interactions within fluids. The polarity forces are much greater and the formation of multimers is observed via hydrogen bonding. How can these specific characteristics be incorporated into an equation of state?

The development of statistical mechanics tools has made it possible to describe the behavior of each intermolecular interaction and has led to a family of equations known as SAFT (Statistical Associating Fluid Theory). IFPEN has been developing a version of this equation for several years:
- proposing a group contribution method enabling the equation to be parameterized for a large number of chemical families;
- adding a specific term for polarity.
In addition, the equation has recently been extended to include electrolytes.

Thanks to this work on the GC-PPC-SAFT[1] equation of state, carried out jointly with Paris XIII University, IFPEN researchers now have access to a tool that can be coupled with process simulators and is capable of reproducing the behavior of phases containing oxygenated products. The complexity of the molecular species encountered in bio-based fluids makes it necessary to further fine-tune the description of the interactions. In particular, new developments aim to describe their solubility in "green" solvents containing salts. This research is being conducted within the context of the Tuck Foundation's "Thermodynamics for biofuels" chair.



Influence of the hydrogen bond (association) on the isothermal phase diagram of an alcohol with a ketone.

S. Tamouza, *J.P. Passarello, P. Tobaly,* ***J.C. De Hemptinne,*** *Fluid Phase Equilibria, 2005, 228-229, p. 409-419.*

D. Nguyen-Huynh, *J.P. Passarello, P. Tobaly,* ***J.C. De Hemptinne,*** *Fluid Phase Equilibria, 2008, 264, No.12, p. 62-75.*

1 - Group Contribution - Polar - Perturbed Chain - Statistical Association Fluid Theory

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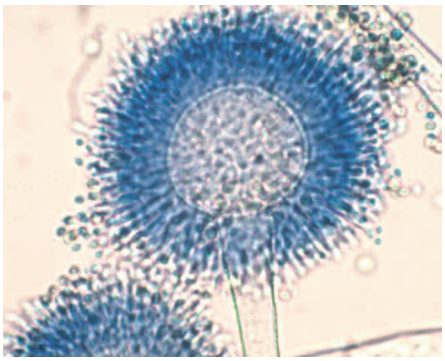
More sugar thanks to enzymes

One of the important stages in the production of 2nd-generation biofuels using biochemical processes is the enzymatic decomposition of lignocellulosic biomass into fermentable sugars. Enzyme mixtures containing cellulases, hemicellulases, beta-glucosidases and other minority enzymes are used to achieve this. However, although they are suitable for this purpose, their efficiency still needs to be significantly improved if the process is to be economically viable.

To this end, the first step was to modify some of the enzymes in the mixture produced by the industrial fungus, *Trichoderma reesei*. In particular, the activity of beta-glucosidase, responsible for the hydrolysis of cellobiose into glucose, has to date been a limiting factor as only low amounts are produced. As part of the ANR HYPAB project, IFPEN researchers, working together with Protéus, have managed to significantly increase the activity of this enzyme using combinatorial molecular engineering techniques. Hence, certain *T. reesei* strains expressing this improved enzyme present a beta-glucosidase activity six times greater than that of the parent strain, and a twofold higher initial hydrolysis rate on wheat straw. It is now possible to use a fourfold lower enzyme load while still maintaining the same hydrolysis yield.

To further improve this result, studies have been conducted to identify new enzymes from other fungi that are complementary to the *T. reesei* enzymes. Hence, as part of the ANR E-Tricel project, the strain collection of INRA's "Biotechnology of filamentous fungi" unit in Marseille was screened. This led to identification of a new enzyme, isolated from the fungus *Aspergillus japonicus*, which, when added to the initial enzyme cocktail, increases the hydrolysis yield by 20%. Studies are under way to further elucidate the mechanism of action of this protein.

Molecular engineering of enzymes and supplementation of the *T. reesei* enzyme cocktail with new enzymes from other strains are two complementary strategies that look very promising. They have already demonstrated their capacity to improve the enzyme cocktail, thereby helping to significantly reduce the cost of the process concerned.



The Aspergillus japonicus fungus seen under the microscope © Bernard CAHAGNIER / Inra.

C. Ayrinhac, ***A. Margeot, N. Lopes Ferreira, F. Ben Chaabane, F. Monot****, G. Ravot, J.M. Sonet, L. Fourage.* Improved Saccharification of Wheat Straw for Biofuel Production Using an Engineered Secretome of *Trichoderma reesei* Organic. Process Research & Development 15, 2011, 275–278. *DOI: 10-1021/op100218a*

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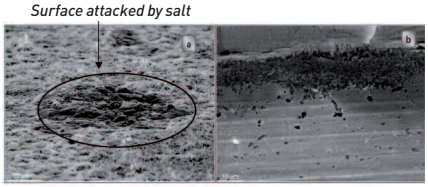
No low-salt diet for refractory steels

The thermochemical process for the production of BtL (Biomass to Liquids) fuels is based on two successive stages: gasification of solid biomass into synthetic gas, followed by a process to convert this gas into a hydrocarbon (Fisher-Tropsch synthesis).

Following the gasification stage, some of the ingredients in the biomass — such as alkaline salts — may be in the form of molten salts, which can damage the metallic walls of reactors. However, little is known about the resistance of refractory steels to corrosion induced by molten salts at 800/1000°C in low oxidizing atmospheres ($PO_2 \approx 10^{-18}$ bar), as encountered with synthetic gas (CO-H_2-CO_2), and this therefore represents an obstacle when choosing the material and also for ensuring the reliability of the processes.

In collaboration with the University of Grenoble (SIMaP laboratory), IFPEN has developed an experimental methodology that consists in characterizing, by thermogravimetric analysis (TGA),the corrosion behavior under salt deposition conditions. This was performed on different metallic alloys in the presence of Na_2SO_4 at 900°C or NaCl at 815°C. The method made it possible to identify HR120 (38Ni-34Fe-25Cr) refractory steel as resistant thanks to its self-healing behavior at 900°C in the presence of Na_2SO_4, with the first addition of Na_2SO_4 leading to the formation of an oxide layer that proves to be protective against subsequent additions (see figure). In addition, our studies performed with the same experimental device, have shown that a preoxidation treatment (at 900°C in a low oxidizing atmosphere) improved the corrosion resistance of this type of steel.

The methodology used revealed the parameters governing the high-temperature corrosion of refractory steels in atmospheres representative of the thermochemical treatment of biomass. It is thus possible to optimize the selection and pretreatments of metallic materials to ensure the reliability of the equipments.



SEM micrographies of HR120 alloy in the presence of Na_2SO_4 after 96 h at 900°C under synthetic gas. a) view inclined at 80°; b) cross section.

L. Couture, ***F. Ropital, F. Grosjean, J. Kittel,*** *V. Parry, Y. Wouters,* Reversible catastrophic oxidation of a 38Fe-34Ni-25Cr alloy induced by sodium sulphate at low oxygen potential atmospheres, *Corrosion Science, 55, 2012, pp 133-139. DOI: 10.1016/j.corsci.2011.10.010*

L. Couture, ***F. Ropital, F. Grosjean, J. Kittel,*** *V. Parry, Y. Wouters,* Influence of the oxygen partial pressure on the high temperature corrosion of 38Ni-34Fe-25Cr alloy in presence of NaCl deposit, *Oxidation of metals, 80, 2013, 5, pp 577-588. DOI: 10.1007/s11085-013-9397-8*

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Better management of batteries aging

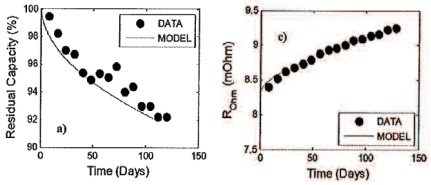
Batteries ensure the reversible storage of electricity in a chemical form. For electric vehicles, the power and energy requirements vary depending on the degree of electrification. Different technologies are used (lead-acid, nickel metal hydride, lithium-ion batteries, etc.) depending on the function: power buffer in the case of a hybrid vehicle, energy source for a plug-in hybrid or all-electric vehicle.

The energy and power of batteries are affected by aging phenomena, which lead to a decreased performance: loss of storage capacity, on the one hand, and increase of the internal resistance, on the other. Knowing how these properties evolve depending on usage is therefore essential in order to define the battery management strategy, or to guarantee battery lifetime and anticipate the evolution in the vehicle's performance.

The aging phenomena involved are multiple, complex and often interlinked. They exist whether the battery is operating (cycle-life aging) or inactive (calendar-life aging).

Numerous studies are being conducted to develop aging models capable of predicting battery life span. Empirical approaches were developed first, as part of joint projects involving IFPEN: SIMSTOCK, SIMCAL[1] and SCOL'ELEC. But the resulting models are limited and difficult to extrapolate. Therefore, IFPEN is examining a complementary physics-based approach: the dominant aging mechanisms are identified and modeled by considering the chemical reactions involved. For example, the electrolyte reduction at the electrode triggers the growth of a deposit that affects the internal resistance. The advantage of such models is their ability to link microscopic and macroscopic properties.

IFPEN already has an electrochemical model for Li-ion battery aging that can be used to optimize battery life span, depending on the vehicle use[2]. This approach is to be extended to another Li-ion battery technology and to other aging mechanisms and it will feed the AMESIm® LIBES battery model library used by the automobile industry.



Simulated and measured evolution of the resistance and capacity of a Li-ion battery-during aging according to a VHR profile. Electrochemical model [2].

*(1) M. Kassem, **J. Bernard, R. Revel,** S. Pélissier, F. Duclaud, C. Delacourt, Journal of Power Sources, Volume 208, 15 June 2012, Pages 296-305. DOI: 10.1016/j.jpowsour.2012.02.068*

*(2) **E. Prada, D. Di Domenico, Y. Creff, J. Bernard, V. Sauvant-Moynot, F. Huet ;** J. Electrochem. Soc. 2013, 160(4): A616-A628. DOI:10.1149/2.053304jes*

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Microfluidics, macroadvantages!

The microfluidic tool, used to control flows on a scale of hundreds of microns, has been the source of numerous scientific advances in a range of fields, from characterization to synthesis, via the selection of organisms or high-throughput screening.

After first emerging in the 1980s, microfluidics saw its popularity increase in the 2000s and have now become a "tool of the trade" in many physicochemistry labs. This is because the method presents a number of very useful characteristics: laminar flows, a high sensitivity to surface phenomena, the possibility of quickly handling tiny volumes. A capacity to precisely determine physicochemical properties, perform fine control of chemical reactions and perfectly control synthesis of dispersions (emulsions, foams) are just some of the resulting advantages.

Furthermore, these systems have dimensions common to a number of biological systems (cells, micro-organisms or even proteins), making microfluidic tool central to the "lab on a chip" revolution.

IFPEN has developed a microfluidic activity incorporating both know-how and original developments. Consequently, its researchers now have access to a laboratory capable of creating prototype microsystems in less than 24 hours! In addition to being used to understand and characterize a variety of physicochemical phenomena, microfluidics is currently employed in various projects aimed at creating solids or developing hight-throughput experimentation for chemical EOR (Enhanced Oil Recovery) and for screening fungal strains intended for the production of 2nd-generation biofuels.

In the particular context of EOR, for example, microfluidics provides access to a suitable scale for understanding complex flows in rocks, as in the case of foam injection. A micro-system can thus simultaneously cover all the processes involved in an unlimited variety of physicochemical conditions, *i.e.* the generation of perfectly controlled foam and the production of detailed information on its evolution and its flow in model confinement situations.

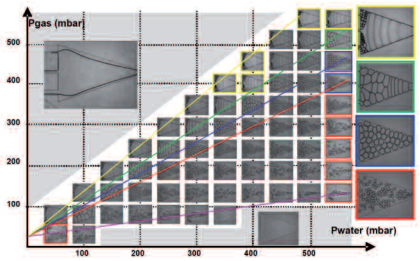

Diagram of foam formation for different water and surfactant pressure and gas pressure conditions.

***N. Quennouz,** M. Ryba, **J.-F. Argillier, B. Herzhaft, Y. Peysson, N. Pannacci,** Microfluidic study of foams flow for Enhanced Oil Recovery (EOR), publication in the journal OGST in preparation.*

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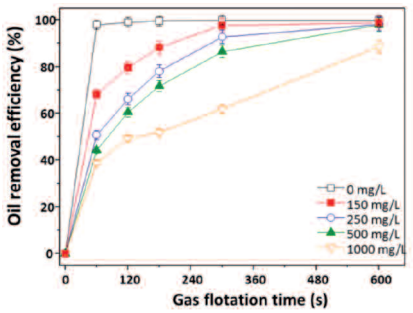
EOR and the water cycle: towards better treatments

Enhanced oil recovery (EOR) plays a key role in increasing the quantity of oil extracted from a field. Within a context of rising oil prices and decreasing fossil resources, EOR is crucial if we are to meet long-term energy needs.

The chemical version of EOR uses viscosifying polymers and surfactants, which are injected into reservoirs, to improve the recovery of oil and gas. One problem that has as yet been little studied is the impact of these products on the produced water cycle. This involves verifying the compatibility of EOR processes with current technologies for treating produced water before it is reinjected.

To this end, IFPEN, working with Petrobras and Statoil, has just conducted a study designed to measure the impact of the additives used in chemical EOR on surface water separation and treatment facilities. A methodology has been developed at the laboratory to reproduce the phenomena observed. The results obtained demonstrate a significant impact of polymers and surfactants on the efficiency of water treatment using flotation or membrane filtration methods. This is because polymers modify the rheological properties of the aqueous phase, while surfactants affect the dynamic interface properties.



Effect of the polymer (hydrolyzed polyacrylamide, concentration of 0 to 1000 mg/l) on the efficiency of oil recovery, for different flotation times.

In the case of a flotation process, involving the injection of gas, surfactants not only induce foaming problems, but also have the effect of stabilizing oil drops, preventing them from coming into contact with the gas bubbles and thereby causing them to rise to the surface more slowly.

For their part, polymers have a rheofluidifying character, causing the bubbles injected to line up like strings of beads, reducing the probability of encountering oil drops.

A better understanding of these complex media, of the physicochemical mechanisms involved and their dynamics is essential to improve current produced water treatment processes.

For this reason, IFPEN launched the Dolphin JIP, an ambitious experimental project, in conditions representative of oil fields. Scheduled to last three years, the project aims to study the impact of chemical EOR on the production system as a whole, and, more specifically, the compatibility of EOR additives with produced water treatment processes.

C. Dalmazzone, C. Noik, J-F. Argillier, Impact of Chemical Enhanced Oil Recovery on the Separation of Diluted Heavy Oil Emulsions, *Energy&Fuels, 2012, 26, 3462–3469. DOI: 10.1021/ef300083z*

J-F. Argillier, C. Dalmazzone, I. Henaut, M. Mouazen, ***C. Noik,*** M. Boufarguine, Methodological Approach for Analyzing the Impact of Chemical EOR on Surface Processes; *OCS Proceedings, The Woodlands, Texas, USA, 8–10 April 2013; SPE Paper 164098.*

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Visiting Scientist

• **Ian Frigaard,** *Professor of Applied Mathematics & Mechanical Engineering at the University of British Columbia (Vancouver, Canada), was IFPEN's visiting scientist from September 2013 to February 2014.*

Award

• **Fabien Chainet,** *a PhD student, received the French Chemistry Society – Analytical Chemistry Division award for his thesis on Silicon Speciation in Hydrotreatment Feeds (January 2014).*

Accreditation to Direct Research

• **Antoine Margeot,** *accredited to direct research at the University of Paris 7 for: "Genetics and Genomics of an industrial filamentous fungus" (January 2014).*

Upcoming scientific events

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Advances in innovative experimental, methodology or simulation tools used to create, test, control and analyse systems, materials and molecules (NEXTLAB 2014) –*** *2-4 April 2014, IFPEN Rueil-Malmaison.*

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Photocatalysis for Energy (PHOTO4E) –*** *15-17 October 2014, IFPEN-Lyon.*

Appointment

• **Dominique Herrier,** *Deputy Director of the Transport Business Unit, was appointed to represent the French Ministry for Higher Education and Research as an expert within the project group for the "Accessible car consuming under 2L per 100km" plan, part of the New Industrial France scheme (December 2013).*

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