Science@ifpen
Issue 20 - April 2015

SPECIAL ISSUE
Understanding reaction mechanisms

Combining scientific research with technological innovation is by no means a simple process, with straightforward pathways existing between the two. The first involves creativity, an almost artistic approach, that can lead the researcher far from his or her initial objective. The second is rooted in reality, in the form of usefulness to society and the presence of a market. And yet it is IFPEN's job to contribute to this continuity. To do so, it is necessary to identify the right targets, as well as the strategies adapted to achieve them. That is the role of the challenge identification policy implemented by IFPEN, supported by the Scientific Board.

Challenge No. 2: "Understanding chemical/catalytic/enzymatic reaction mechanisms on a molecular scale" is of strategic importance. Closely linked to both characterization and modeling, this work should help us grasp the complexity of phenomena, in order to develop robust processes and reliable products, upon which IFPEN's success depends.

This issue of Science@ifpen shows the diversity of topics examined from the angle of this challenge.

I hope you enjoy reading this issue.

Bruno Chaudret
Member and former Chairman of IFPEN's Scientific Board
Member of the French Academy of Sciences

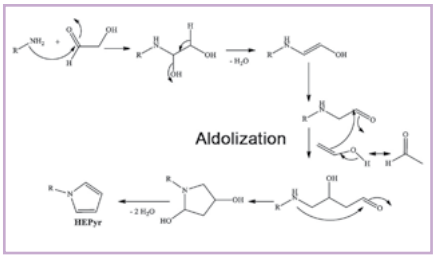
CO_2 capture: what impact for the environment?

The aim of CO_2 capture in industrial flue gases is to limit greenhouse gas emissions into the atmosphere. Nevertheless organic products (amines) used in capture processes degrade more or less to generate new substances, which maybe potentially harmful to the environment. How can we predict which degradation products would form from an amine selected to effectively capture CO_2 at low cost? This is the question IFPEN scientists set out to answer through their research in this field.

First of all, the degradation of a whole range of amines was studied. Their relative chemical stabilities were explained and the different types of chemical reactions leading to the formation of the main degradation products were identified[1].

The researchers then focused on a model amine substance (ethanolamine or MEA), making it possible to identify products potentially present — albeit it in trace amounts — in the gaseous effluent of the process. These are chemical families that are totally unknown in this context: pyrazines, oxazolines, oxazolidines, pyrroles[2] and pyridines. The list of the types of chemical reactions liable to affect the amines was thus extended: in particular, aldolization, which very clearly explains the elongation of the initial substance's carbon chain (see Figure).

This identification and elucidation work helped constitute a tool box identifying the chemical reactions applicable to amines in CO_2 capture conditions, on the basis of their chemical structure. So, the developers of these technologies can anticipate the nature of the degradation products and take appropriate counter-measures if necessary.



Mechanism for the formation of pyrroles including an aldolization step.

(1) ***H. Lepaumier,*** *D. Picq,* ***P.-L. Carrette,*** *Ind. Eng. Chem. Res., 2009, 48, 9061. DOI: 10.1021/ie900472x*

(2) ***C. Gouedard,*** *A. Rey, V. Cuzuel, J. Brunet, B. Delfort, D. Picq, J. Dugay, J. Vial, F. Launay,* ***L. Assam, J. Ponthus, P.-L. Carrette,*** *International Journal of Greenhouse Gas Control, 2014, 29, 61-69. DOI: 10.1016/j.ijggc.2014.07.013*

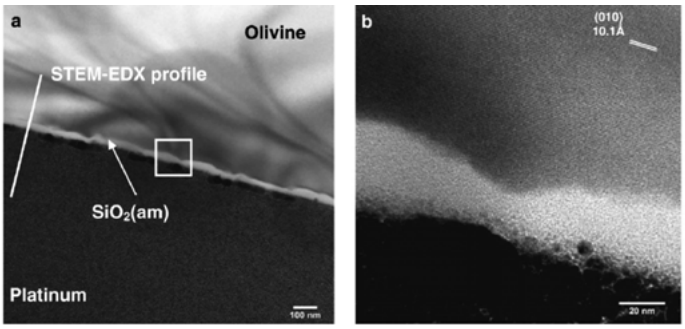
Scientific contact:
p-louis.carrette@ifpen.fr

CO_2 mineralization: a rebounding topic?

To reduce the greenhouse effect related to CO_2 emissions, one of the solutions aims to reproduce a millennia-old natural mechanism: carbonation. Once injected to extreme depths, under high pressure and temperature conditions, the CO_2 dissolved in water interacts with rocks, accelerates the alteration of silicate minerals with a high Mg, Fe, Ca content and promotes the formation of new phases trapping carbon in solid form.

Basic and ultrabasic rocks, in which the highly reactive minerals have a low silica content but a high iron and magnesium content, are excellent candidates for this process, such as olivine ($[Mg,Fe]_2SiO_4$), for example. The factors liable to affect the dissolution of this mineral were therefore studied[1] by IFPEN scientists.

Research was conducted jointly with the CNRS (IPGP, ISTErre, LHyGeS, ENS) in a laboratory reactor to simulate underground conditions[2]. These studies revealed the formation of nanometric layers of silica on the surface of the olivine, which significantly slowed down the transport of species in solution, thereby preventing the formation of carbonates.



Nanometric silica layer passivating the mineral surface, observed by ETM[2].

However, on these iron (III)-rich layers of silica, this passivating effect only appears to occur in oxidizing conditions[3]. (Partial) oxygen pressure P_{O_2} therefore appears to play a crucial role, suggesting a correlative role of any auxiliary gases present in the gas injected, such as NOx or H_2S.

Although large-scale CO_2 storage using this method has not been the subject of significant investment up to now, a clear understanding of the oxidation-reduction mechanisms involved made it possible to consider other reaction processes open to potential CO_2 conversion, as part of a thesis work.

(1) ***B. Garcia, V. Beaumont, E. Perfetti, V. Rouchon, D. Blanchet,*** *et al., AppGeochem, 2010, 25(9), 1383-96.*

(2) D. Daval, ***O. Sissmann,*** (...), ***B. Garcia,*** et al., *ChemGeol, 2011, 284, 193–209. DOI: 10.1016/j.chemgeo.2011.02.021.*

(3) ***O. Sissmann,*** *F. Brunet, I. Martinez (...) D. Daval et al., EnvSciTech, 2014, 48 (10), 5512–5519. DOI: 10.1021/es405508a*

Scientific contacts:
olivier.sissmann@ifpen.fr
bruno.garcia@ifpen.fr

A clearer understanding of fuel stability for a better fluid modeling

Designing innovative, clean and optimized fuels for IC engine vehicles requires a sound knowledge of the reaction mechanisms involved, particularly those related to their oxidation during storage.

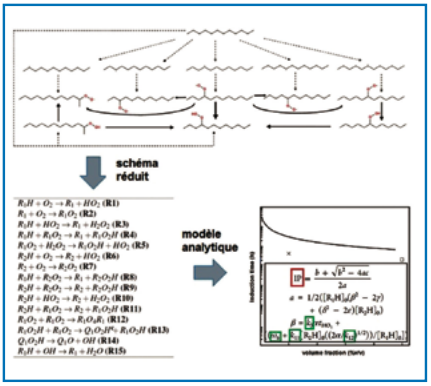
To model oxidation, the reaction classes to be considered in kinetic diagrams are increasingly numerous. In the 1980s, this led to the development of automatic mechanism generators, a trend that has since been accentuated due to the rapid development of fuel formulations.

However, liquid-phase oxidation, which involves more mechanisms than in gas phase, is complicated by the effect of the solvent on the reaction kinetics, making it even more difficult to use digital tools in this context.

Studies carried out by IFPEN researchers have recently led to the development and validation of an approach based on several steps: determination of model fuels (surrogates), generation of kinetic diagrams for these surrogates using open source RMG code, their validation on experimental data and, finally, reduction of the model by analysis of the reaction processes.

These studies, focusing on the issue of stability to oxidation and based on a deductive methodology (see Figure), pave the way for the industrialization of *in silico* fuel design methodologies[1]. They are continued using *ab initio* calculations in order to fine-tune the most important reaction parameters within the reaction process.

In addition, modeling using an inductive approach was implemented to monitor the macroscopic indicators of fuel oxidation.



Overview of the modeling approach.

(1) ***A. Ben Amara, A. Nicolle, M. Fortunato and N. Jeuland,*** *Energy Fuels, 2013, 27, 6125–6133. DOI: 10.1021/ef401360k*

(2) ***A. Ben Amara, A. Nicolle, P. Hayrault, L. Starck and N. Jeuland,*** *Conference of the International Association for Stability, Handling and Use of Liquid Fuels, 2013.*

Scientific contacts:
arij.ben-amara@ifpen.fr
andre.nicolle@ifpen.fr

Sulfide catalysts hunt down the oxygen in bioresources

To limit the carbon footprint of fuels or chemical intermediates, the substitution of fossil resources by renewable ones is a promising routes (vegetable oils, animal fats, pyrolysis oils, lignin, etc.).

One of the specific characteristics of these substances is their high oxygen compound content, something that is often incompatible with the properties and specifications of the target products. It is therefore necessary to process these bioresources using a catalytic treatment to eliminate — either partially or totally — the oxygen they contain.

For hydrotreatment, nickel-promoted molybdenum sulfide (NiMoS) catalysts are highly versatile and enable the purification and conversion of hydrocarbons of either fossil or biomass origin.

Thanks to close collaboration with IRCELYON[1-2], and combining an experimental kinetic approach with quantum molecular modeling, IFPEN has identified the reaction mechanisms involved in the deoxygenation of model molecules used on an active site scale. The key role of the promoter (Ni) on deoxygenation and decarbonylation activity and selectivity has thus been demonstrated. This paves the way for further optimization of catalyst formulations.

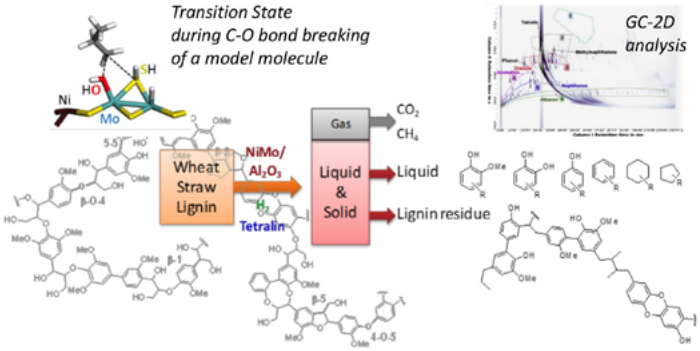


Diagram of the lignin conversion.

More recently, thanks to a multi-technical approach (based on two-dimensional chromatographic analysis), further progress has been made in terms of our understanding of the mechanisms and steps involved in the conversion of complex oxygenated feeds[3]. This research, conducted on lignin, should help scientists manage the reaction conditions in order to control its conversion into valuable chemical products (aromatics or phenols).

(1) ***C. Dupont, R. Lemeur, A. Daudin, P. Raybaud.*** *J. Catal., 2011, 279, 276, DOI: 10.1016/j.jcat.2011.01.025*

(2) ***M. Ruinart, C. Dupont, A. Daudin, P. Raybaud,*** *C. Geantet, J. Catal., 2012, 286, 153, DOI: 10.1016/j.jcat.2011.10.022*

(3) ***B. Joffres,*** *C. Lorentz,* ***M. Vidalie,*** *D. Laurenti,* ***A-A. Quoineaud, N. Charon, A. Daudin, A. Quignard,*** *C. Geantet, Appl. Catal. B: Env., 2014, 145, 167. DOI: 10.1016/j.apcatb.2013.01.039*

Scientific contact:
antoine.daudin@ifpen.fr

The genome of a fungus decyphered

The production of ethanol from lignocellulosic biomass includes an hydrolysis step, which uses an enzyme cocktail produced by a filamentous fungus, *Trichoderma reesei.* Enzymes are expensive to produce and more productive strains reduce the investment required.

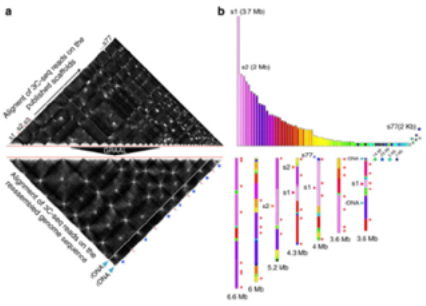
Progress of this type depends on a sound understanding of how current strains work, gained by decyphering their entire genome.

In a first study[1], thanks to spectacular progress in the field of DNA sequencing, the genome of two strains of *T. reesei* was exhaustively "read" and their mutations relative to the natural isolate were identified. However, the technique only enabled small changes to be observed.

In a new study conducted jointly by IFPEN with a team from the Pasteur Institute[2], the spatial environment of the genes was "captured" and analyzed. Hence, each gene was repositioned on its chromosome, making it possible to characterize the latter's spatial configuration.

It emerged that, despite being located on different chromosomes, the genes important for the production of enzymes are grouped together spatially, which may explain the productivity of the fungus. It was also shown that the chromosomes of the strains have undergone major chromosomal rearrangements compared to the natural isolate.

These results open up major new avenues for the understanding of gene regulation in fungi and offer a new study angle to improve the performance of industrial strains.



Raw data from the DNA sequencing of T. reesei *(top), and rearranged (bottom) into seven chromosomes (bottom, right) and into physical proximity data (bottom, left).*

(1) *S. Le Crom, (...),* ***A. Margeot,*** *Proc. Natl. Acad. sci USA, 2009, 106(38), 16151–6. DOI: 10.1073/pnas.0905848106*

(2) *H. Marie-Nelly, (...),* ***D. Poggi Parodi,*** *(...),* ***A. Margeot,*** *C. Zimmer, R. Koszul, Nature Communications, 2014, 5, 5695. DOI: 10.1038/ncomms6695*

Scientific contact:
antoine.margeot@ifpen.fr

The Li-ion awakes tonight

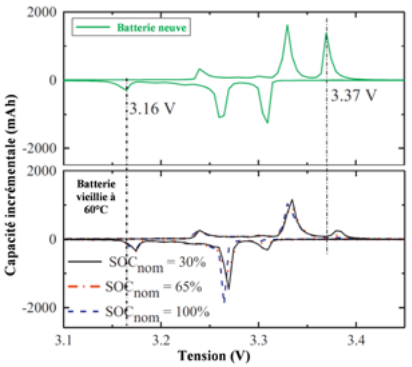
Li-ion batteries, which provide reversible energy storage for electric vehicles, are subject to multiple, complex and often inter-dependent aging mechanisms, which have an impact on vehicle performance. Understanding this aging, on the basis of vehicle use, is essential to define the electric and thermal management strategy for the battery and to guarantee its lifespan.

The empirical models currently developed are limited and difficult to extrapolate. So IFPEN is examining a complementary, more theoretical, approach, in which the aging mechanisms are modeled on the basis of the chemical reactions involved.

To implement this approach, the dominant mechanisms need to be identified and understood. One of the difficulties is that a macroscopic consequence, such as loss of capacity, can be the result of different phenomena: the loss of cyclable lithium *via* trapping in a degradation deposit or the loss of active matter by degradation of the electrodes. Since the battery is a closed system, the measurable values are also limited (voltage, current, temperature).

In the context of the Simcal network[1], specific measurements were used, such as electrochemical impedance spectroscopy or the PITT (Potentiostatic Intermittent Titration Technique) method to characterize batteries aged to varying degrees (see Figure) and hence provide information on the phenomena. In addition, *post-mortem* examinations were conducted to confirm and supplement this information[2]. Batteries at the end of their life were dismantled and each of the electrodes were reassembled in button battery format to study them separately. Samples of the different components were also analyzed (SEM, XRD, etc.) to characterize the evolution of materials.

Once identified, the aging mechanisms will be incorporated in behavioral physical models. These studies pave the way for new tools to diagnose the state of Li-ion batteries and, ultimately, management strategies.



Incremental capacity curves derived from PITT measurements for LFP/C batteries in initial condition and aged at 60°C.

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

(2) ***J. Bernard, R. Revel,*** *BATTERIES Proceedings, NICE, 2013.*

Scientific contact:
julien.bernard@ifpen.fr

News

Winner of the 2005 Nobel prize in Chemistry, engineer and Director of Research at IFPEN from 1960 to 1995, Yves Chauvin died on 27 January 2015. His research led to the emergence of a world-renowned French school of homogeneous catalysis and resulted in industrial developments that contributed to a more sustainable approach to chemistry. On 21 January 2015, Yves Chauvin was awarded the Grand Cross of the French National Order of Merit. A final tribute to a scientist whose pioneering spirit, passion, perseverance, genius and modesty led him to the very highest levels of his discipline.

Award

On 16 December 2014, Florence Delprat-Jannaud, coordinator of the European SiteChar project on the characterization of geological CO_2 storage sites, was awarded one of the 12 Étoiles de l'Europe 2014. *The European project, led by IFPEN, included geoscience modeling, economic calculations, along with a communication component dedicated to societal aspects.*

Upcoming scientific events

- *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– LowPerm2015 –*** *9-11 June 2015, IFPEN Rueil-Malmaison - www.rs-lowperm2015.com*
- *SCF "Chemistry and energy transition" meeting – 4-9 June 2015, Lille*
- *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Microfluidics –*** *4-5 November 2015, IFPEN Rueil-Malmaison - www.rs-microfluidics2015.com*
- *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– SimRace –*** *8-10 December 2015, IFPEN Rueil-Malmaison - www.rs-simrace.com*

Publications

- *OGST – IFP Energies nouvelles Journal – Issue 1, volume 70 (2015) – Issue dedicated to the E-COSM'12 Workshop on Engine and Powertrain Control, Simulation and Modeling. (http://ogst.ifpenergiesnouvelles.fr)*

HDR

- ***Bruno Garcia,*** *HDR at Bordeaux Montaigne University: "Contribution to understanding the impact of CO_2 injection in geological environments: the geochemistry of fluids, from reservoir to surface."*
- ***Fadhel Ben Chaabane,*** *HDR at the Institut National Polytechnique (INP) in Toulouse. His research focused on the development of rational approaches to optimize fermentation processes.*
- ***Nicolas Lopes Ferreira,*** *HDR at Paris Diderot-Paris 7 University. His research focused on improving the enzymatic hydrolysis of lignocellulosic biomass.*

Managing Editor: Marco De Michelis
Editor-in-chief: Éric Heintzé
Editorial committee: Xavier Longaygue, Laurent Forti, Françoise Brucy
Graphic Design: Esquif
ISSN No. 1957-3537

To get in touch with IFPEN or receive Science@ifpen:
Institutional Relations and Communications Division:
Tel.: +33 1 47 52 51 34 - Science@ifpen.fr
1 et 4, avenue de Bois-Préau - 92852 Rueil-Malmaison Cedex - France
Press contact: A.-L. de Marignan - Tel.: +33 1 47 52 62 07 – **Institutional contact:** A. Sanière - Tel.: +33 1 47 52 69 19