Science@ifpen
Issue 15 - November 2013

Microorganisms change their diet*

Thesis by Étienne Jourdier, 2013 Yves Chauvin prize-winner

IFPEN's policy of hosting PhD students forms one of the pillars of our scientific strategy. It gives students an opportunity to consolidate their training by carrying out advanced research and by working within an applied context, with an opening towards industry and future career opportunities.

From our point of view, it is a way of advancing our expertise and approaching original avenues for progress in order to overcome obstacles that have been identified in our innovation areas. This policy also helps to forge or strengthen links with academic research — in France and throughout Europe — and expands the network of scientific resourcing available to our researchers.

This year, the Scientific Board awarded the Yves Chauvin prize to Étienne Jourdier for his research on the "production of cellulases by Trichoderma reesei for lignocellulosic biorefineries". During its deliberations, the Board praised the theoretical and experimental quality of the research, along with its major contribution to IFPEN's R&D potential in the field of biotechnologies.

We hope that you enjoy this issue,

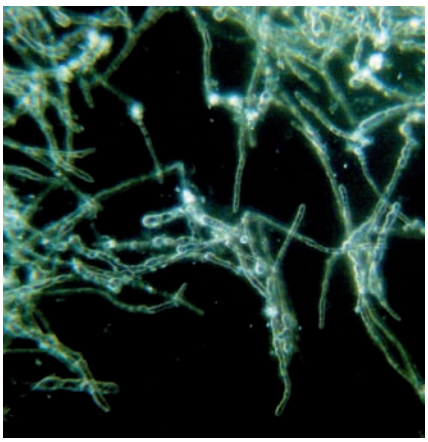
Pierre-Henri Bigeard,
Executive Vice-President

Since they use lignocellulosic biomass, second-generation (2G) biofuels do not compete with food uses and have a better CO_2 balance than fossil fuels.

Technical and economic studies have shown that the enzymes required to hydrolyze biomass (cellulases) represent a significant obstacle to the industrial development of 2G bioethanol production processes due to their high cost price. One idea to bring this cost down is to produce the cellulases at the biomass pre-treatment site, particularly using by-products of this process, such as carbon substrates, for example. The effect of these carbon sources on the metabolism of the enzyme-producing microorganisms thus had to be determined. *Trichoderma reesei* is the microorganism selected for this study due to its high enzyme-secreting capacity.

The study was conducted in two stages: first of all, the stoichiometry of the reactions was determined, both for cellular growth and for enzyme production, and then a kinetic study was conducted to quantify and model the microorganism's behavior.

The results obtained have significantly enhanced the model for understanding the metabolism of *T. reesei*. In addition, original models incorporating industrial constraints have been developed in order to constitute rational tools to help define a cellulase production process integrated into a lignocellulosic biorefinery.



Trichoderma reesei seen under an optical microscope (magnification x 40).

* Thesis entitled: **Modeling and optimization of cellulase production by *Trichoderma reesei* for lignocellulosic biorefineries**

E. Jourdier, L. Poughon, C. Larroche, F. Monot, and F. Ben Chaabane, A new stoichiometric miniaturization strategy for screening of industrial microbial strains. *Microb Cell Fact 11, 2012, 70.*
DOI: 10.1186/1475-2859-11-70

E. Jourdier, C. Cohen, L. Poughon, C. Larroche, F. Monot, and F. Ben Chaabane, Cellulase activity mapping of Trichoderma reesei cultivated in sugar mixtures. *Biotechnol Biofuels, 2013, 6,79.*
DOI: 10.1186/1754-6834-6-79

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Unmasking oxygen*

Thesis by Badaoui Omais

The direct liquefaction of lignocellulosic biomass by fast pyrolysis, catalytic pyrolysis, hydrothermal conversion, etc. is a promising avenue — although still in the development phase — for the production of biofuels and biobased products. However, the bioliquids obtained are oxygenated, unlike fossil-derived products. Their molecular characterization is therefore crucially important in order to optimize processes as well as the innovative catalytic systems that will be applied to them.

Oxygen speciation in these hydrocarbon matrices represents a real analytical challenge since they are complex mixtures, with a very broad diversity of chemical structures and polarities. Their detailed analysis demands a multi-method approach, involving, in particular, selective, high-resolution gas chromatography techniques.

The research work carried out has revealed the full potential of two-dimensional gas chromatography (GC x GC) for the detailed analysis of oxygen compounds (alcohols, phenols, carboxylic acids, ketones, etc.) contained in partially deoxygenated biomass pyrolysis oils containing 100 to 200 g/kg of oxygen. It should be noted that as part of this thesis, the method was also successfully used for coal-derived liquids having a lower oxygen content (5 to 10 g/kg).

Consequently, this characterization by GC x GC has been incorporated into a multi-method analytical approach including NMR, mass spectrometry and UV-Vis spectroscopy.

This development of tools and associated expertise in the field of chemical analysis is leading to a better understanding of the composition of products resulting from the processes currently being developed at IFPEN for the conversion of lignocellulosic biomass.

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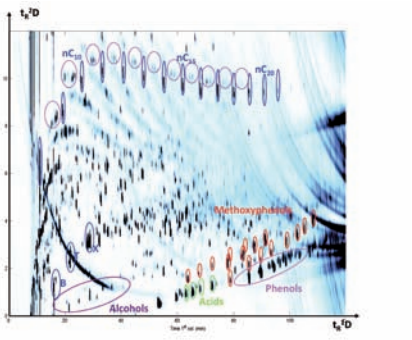

GC x GC-FID chromatogram of a partially deoxygenated pyrolysis oil (on the x and y axes: retention times in seconds of the Solgelwax and RTX200 columns, respectively).

* Thesis entitled: **Oxygen speciation in products derived from the conversion of coal and biomass**

B. Omais, J. Crepier, N. Charon, M. Courtiade, A. Quignard, *D. Thiébaut,* Oxygen speciation in upgraded bio-oils by GC×GC. *Analyst, 2012, 138, 2258-2268. DOI: 10.1039/c2an35597c*

B. Omais, N. Charon, M. Courtiade, J. Ponthus, *D. Thiébaut,* A novel analytical approach for oxygen speciation in coal-derived liquids. *Fuel, 2013, 104, 805-812. DOI: 10.1016/j.fuel.2012.04.04.9*

Catalysts poisoned by silicon: the investigation progresses!*

Thesis by Fabien Chainet

The identification and quantification (i.e. speciation) of species liable to poison refining catalysts in oil products is a real analytical challenge. These species include substances generated by the degradation of polydimethylsiloxane (PDMS) used as antifoaming. To date, the poisoning mechanisms have been poorly understood since knowledge was based on tests solely involving model molecules. The main issues are the presence of silicon in trace amounts (ppb to ppm) and in complex matrices liable to change quickly.

An innovative study was conducted, combining three original actions in the field of speciation: a PDMS degradation experiment in real conditions and at high temperature in a specially adapted pilot plant, storage under liquid nitrogen of the samples produced in order to prevent them evolving, and a multi-technical approach based on advanced analytical tools (GC/MS, SECICP/MS, FT-ICR/MS, GC-ICP/MS, etc.). More than hundred substances from twelve different chemical families were characterized in this way. The presence of silica species has been demonstrated in all oil cuts. Some of the molecules, characterized for the first time in trace amounts, possess reactive functions able to react with the catalyst very rapidly and potentially cause its deactivation.

These original results open up new avenues for understanding poisoning mechanisms and eliminating the substances responsible.

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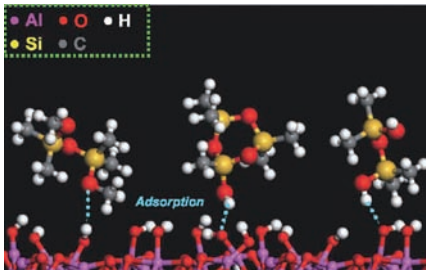

Possible poisoning of an Al_2O_3 catalyst support due to adsorption of reactive silicon molecules.

* Thesis entitled: **Silicon speciation in hydrotreatment feeds**

F. Chainet, J. Ponthus, C.P. Lienemann, M. Courtiade, *O.F.X. Donard. Anal. Chem. 2012, 84, 3998.*

F. Chainet, L. Le Meur, M. Courtiade, C.P. Lienemann, J. Ponthus, *O.F.X. Donard. Fuel, 2014, 116, 478.*

Reducing engine pollution without delay*

Thesis by Delphine Bresch-Pietri

Burned gas recirculation systems and after-treatment systems are two solutions capable of significantly reducing the pollutant emissions of gasoline vehicles.

However, such systems are difficult to manage in real-time. First of all, the distance between onboard sensors on mass-produced engines generates measurement delays relative to physical phenomena. Secondly, matter flows in the numerous pipe circuits present on an engine are subject to transport delays. Furthermore, these time delays are uncertain and, more importantly, variable.

The difficulties resulting from this variability are well known and have long been catalogued. Until now, they have been ignored or tackled using heuristic methods that are highly inadequate in practice, but it has emerged that delay compensation techniques based on the principle of prediction may be able to offer an attractive alternative.

In this research focusing on engine control, the two problems were resolved using a new adaptive control method with distributed parameters. This approach provides the missing link between theory and practice since it makes it possible to process the *ad hoc* solutions developed by engineers in the field within a unified context, at the same time proposing concrete and applicable improvements to these solutions.

The methods proposed, validated both theoretically and by experience, have led to significant savings in terms of response times, as well as improvements in control robustness, with no additional cost or complexity. Thanks to other research carried out jointly at IFPEN, burned gas recirculation systems and after-treatment systems are now moving towards their full use potential.

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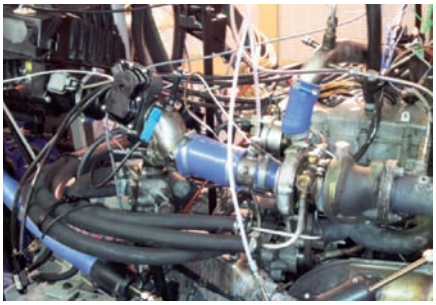


Gasoline engine equipped with a burned gas recirculation circuit.

* Thesis entitled: **Robust control of variable delay systems. Theoretical contributions and applications for engine control**

D. Bresch-Pietri, J. Chauvin, *and N. Petit,* Adaptive control scheme for uncertain time-delay. *Automatica, 2012, 48, 8.*

D. Bresch-Pietri, T. Leroy, J. Chauvin *and N. Petit,* Practical delay modeling of externally recirculated burned gas fraction for Spark-Ignited engines. Delay Systems: From Theory to Numerics and Applications. *Advances in Delays and Dynamics, 2014, 1, 359-372.*

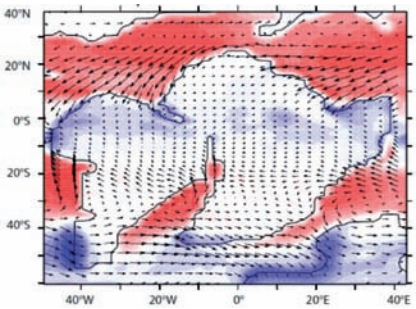
Arid zones on the Equator?*

Thesis by Anne-Claire Chaboureau

Understanding the formation of sediments that are a source of oil reservoirs is a major challenge from the point of view of oil resource discovery and production. Over the course of geological periods, a paradox suggests the existence of extensive arid zones located close to the Equator.

To analyze this geological anomaly and its consequences, the research conducted consisted in integrating the climatic factor with our current understanding of how sedimentary basins are filled.

To do this, an innovative methodology integrating the results of climatic models was developed, in order to better constrain sedimentary system models. Implemented in the South Atlantic scenario, it demonstrated the crucial importance of climate — as well as tectonics — on the dynamics of sedimentary systems during the opening of their basins.



Results of a climate model.

This research made it possible to integrate new parameters resulting from climatic models in order to better constrain our basin software and acquire expertise in a theme that is generating significant interest in the worlds of academic research and industry: the dynamics of the Earth's past climates.

The implementation of the methodology developed is completely unique. It will be possible to apply the method to the characterization of factors leading to the formation of source rocks, for periods traditionally considered to be favorable to the production of organic matter as well as periods considered to be unfavorable.

* Thesis entitled: **Impact of climate and tectonics on the dynamics of sedimentary systems during opening of the South Atlantic**

A.-C. Chaboureau, *Y. Donnadieu, P. Sepulchre, C. Robin, F. Guillocheau,* ***S. Rohais,*** The Aptian evaporites of the South Atlantic: a climatic paradox? *Climate of the past, 2012, 8, 1047-1058.*

A.-C. Chaboureau, *F. Guillocheau, C. Robin,* ***S. Rohais,*** *D. Aslanian, M. Moulin,* Paleogeography of the Central segment of the South Atlantic opening. *Tectonophysics, in press, 2012.*

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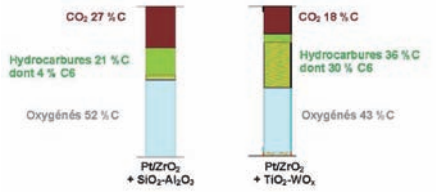
Biomass in the tank*

Thesis by Léa Vilcocq

In the quest to find sustainable alternatives to fossil energies for fuel production, the conversion of lignocellulosic biomass is a promising option.

Converting sorbitol — the sugar alcohol of glucose — directly into light alkanes by aqueous-phase heterogeneous catalysis is one of the avenues being explored. However, the reference catalytic system, based on platinum applied to an oxide, demonstrates a lack of stability in the aqueous phase, as well as deficient silica-alumina acid phase activity.

Furthermore, the reaction produces a multitude of products in addition to the alkanes sought. Titanium oxide-based solids spiked with tungsten have been shown to be stable and active during catalytic tests in reaction conditions. Combined with a metal phase (platinum), these catalysts improve C_5/C_6 alkane selectivity.



Distribution of products resulting from the conversion of sorbitol in aqueous medium on the reference catalytic system (on the left) and the newly developed system (on the right).

Detailed study of the products generated and the use of model molecules from reaction intermediates as reagents have also shed light on the mechanisms involved.

This research has provided IFPEN with some key information concerning the stability and activity of bifunctional heterogeneous catalysts in aqueous medium. The analytical methodology and the test for characterization of acidity in liquid water that were developed are currently being used in projects focusing on the conversion of biomass into bioproducts.

Research is now continuing in order to improve the hydrogenating function.

* Thesis entitled: **Transformation of polyols in aqueous phase by bifunctional heterogeneous catalysis**

L. Vilcocq, A. Cabiac, *C. Especel*, ***S. Lacombe,*** *D. Duprez*, Sorbitol transformation in aqueous medium: influence of metal/acid balance on reaction selectivity. *Catalysis Today, 2012, 189, 117-122. DOI: 10.1016/j.cattod.2012.03.051*

L. Vilcocq, A. Cabiac, *C. Especel*, ***S. Lacombe,*** *D. Duprez*, Study of the stability of Pt/SiO_2–Al_2O_3 catalysts in aqueous medium: Application for sorbitol transformation. *Catalysis Communications, 2011, 15, 18-22. DOI: 10.1016/j.catcom.2011.08.002*

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Pollution abatement in vehicles: from atom to catalytic converter*

A Thesis by Nikola Rankovic

The impact of nitrogen oxides (NOx) — primarily produced during combustion — on both the environment and health has led car manufacturers to equip vehicles with catalytic converters. Since three-way catalysis is not effective for lean-burn engines, NOx traps have emerged as a promising technology for reaching the emission levels required by future regulations.

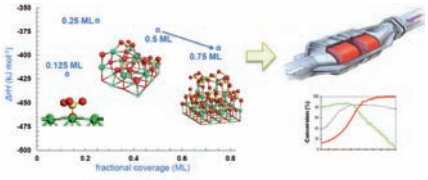
However, the complexity of the mechanisms involved in these systems and the poor level of understanding of their operation makes their design and control extremely difficult.

IFPEN has developed an innovative methodology consisting in transposing the chemical information obtained on an atomic scale, by quantum calculations, into a global industrial simulator used to design after-treatment systems.

The model obtained takes into account the coupling between mass transfer processes and chemical kinetics involved during NOx storage and reduction phases in the presence of complex exhaust streams.

The model predictions of the adsorption-induced reorganization of the crystalline structure of the storage material, are qualitatively consistent with the spectroscopic measurements carried out on a commercial NOx trap. This chemical information globalization methodology — unique of its kind in the world — is a promising approach for optimizing industrial catalysts and controlling NOx traps operation.

A better description of catalyst poisoning could also lead to a reduction in the precious metals loading in after-treatment systems.



Overview of the chemical information globalization method.

* Thesis entitled: **Multi-scale modeling in environmental catalysis: application to the NOx trap**

N. Rankovic, C. Chizallet, A. Nicolle, *P. Da Costa, Chemistry – A European Journal, 2012, 18(34), 10511-10514. DOI: 10.1002/chem.201103950*

N. Rankovic, A. Nicolle, D. Berthout, *P. Da Costa, Topics in Catalysis, 2013, 56(1-8), 140-144. DOI : 10.1007/s11244-013-9943-2*

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Microorganisms in a stir*

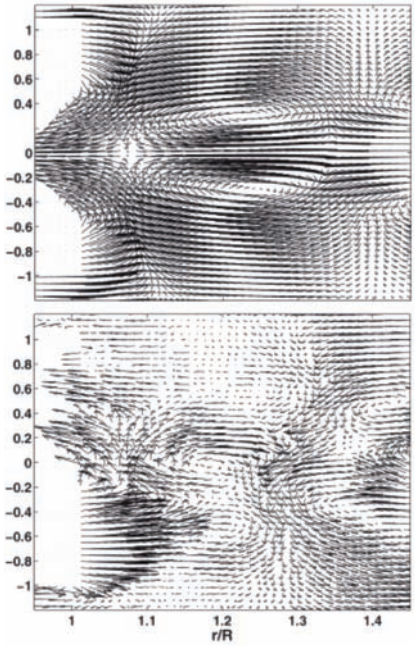
Thesis by Jean-Christophe Gabelle

The production of enzymes by a filamentous fungus *(T. reesei)* is a key step in the production process for second-generation bioethanol.

The fungus is grown in large fermenters, the design of which is problematic due to the complex rheology of the medium in question, which causes a deterioration in oxygen transfer and fluid mixing efficiency.

This problem was tackled by studying the effect of rheology on fermenter operation, using model fluids with representative rheologies. The hydrodynamics and transfer were characterized locally and globally, employing a variety of specific metrological methods: measurement using O_2 sensors, particle image velocimetry (PIV), high-speed camera recording, image-processing. Rheological models were then produced from these measurements.

These models are already being used to define certain parameters when designing industrial fermenters. Study of shear rates has also demonstrated the value of POD (proper orthogonal decomposition) after-treatment. This method reveals the different scales of their fluctuations that may influence the morphology of microorganisms cultivated in stirred tanks.



Coherent and turbulent structures in stirred tanks (PIV-POD method).

The study being launched at IFPEN concerning the behavior of *T. reesei* in hydrodynamic conditions even closer to industrial reality will be based on the prediction of these models (scale-down approach).

* Thesis entitled: **Local and global analysis of hydrodynamics and matter transfer in fluids with a complex rheology characteristic of fermentation media**

J.-C. Gabelle, E. Jourdier, *R. Licht,* ***F. Ben Chaabane, I. Henaut,*** *J. Morchain,* ***F. Augier,*** Impact of rheology on the mass transfer coefficient during the growth phase of *Trichoderma reesei* in stirred bioreactors. *Chem. Eng. Sci, 2012, 75, 408-417.*

J.-C. Gabelle, F. Augier, *A. Carvalho, E. Rousset, J. Morchain,* Effect of Tank Size on kLa and Mixing Time in Aerated Stirred Reactors With Non-Newtonian Fluids. *Can. J. Chem. Eng., 2011, 89.*

J.-C. Gabelle, J. Morchain, *D. Anne-Archard,* ***F. Augier,*** *A. Liné,* Experimental Determination of the Shear Rate in a Stirred Tank with a Non-Newtonian Fluid: Carbopol. *AIChE J., 2013, 59, 6, 2251-2266.*

A. Liné, ***J.-C. Gabelle,*** *J. Morchain, D. Anne-Archard,* ***F. Augier,*** On POD analysis of PIV measurements applied to mixing in a stirred vessel with a shear thinning fluid. *Chem. Eng. Res. Des., 2013. DOI: 10.1016/j.cherd.2013.05.2002*

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Nominations

• **Pascal Barthélemy,** *Executive Vice-President of IFPEN, has been appointed Project Manager for the "Green Chemistry and Biofuels" industrial program by the French Ministry for Industrial Renewal (12 September 2013).*

• **Hélène Olivier-Bourbigou,** *from IFPEN's Catalysis and Separation Division, has been elected President of the Catalysis Division of the French Chemistry Society (28 October 2013).*

Awards

• *IFPEN has earned a place in Thomson-Reuters' list of Top 100 Global Innovators for the third year running.*

• *Two projects involving IFPEN are among the winners of the Predit prizes (7 October 2013): InterMAC (model for better prediction of heat flows linked to the flame-wall interaction in spark ignition engines) and Hydole (plug-in electric hybrid vehicles).*

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.*

HDR

• **Ludovic Raynal,** *HDR at the Institut national polytechnique de Toulouse for his research focusing on the study of hydrodynamics and mass transfer within filled columns using a multiscale approach (27 September 2013).*

• **Alexandra Chaumonnot**, *HDR at UPMC (Pierre et Marie Curie University): "Synthesis and development of oxide-based materials: from existing industrial catalysts towards the design of breakthrough catalysts" (21 October 2013).*

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