Science@ifpen

Issue 17 - July 2014

SPECIAL ISSUE
Characterization of materials and fluids for energy
High-impact publications

A proactive, inventive and productive scientific approach remains the best way to optimize the development of new energy technologies. IFPEN has identified nine scientific challenges that have to be overcome in the ideal development plan for these technologies: they focus our research efforts and guide our academic partnerships.

The first of these challenges is the characterization (operando, on relevant scales, online, etc.) of environments, products and materials for energy. If we can better visualize, represent and quantify catalytic or chemical or enzymatic processes, combustion, the genesis of fluids in natural environments or biomass at various stages in its conversion process, we should be able to conceive acceptable, controlled and optimized energy processes.

Some of IFPEN's contributions to advancing knowledge in these areas are illustrated in this issue, through examples taken from publications that have been broadly cited by the scientific community.

We hope that you enjoy reading all about them.

Jacques Jarrin
Director, Scientific Division

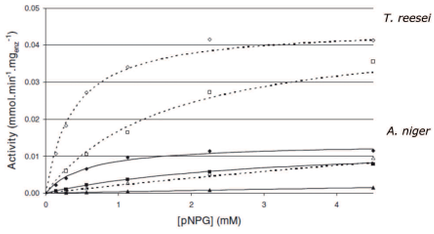
One model for two (enzymes)

Producing biofuels from lignocellulosic biomass requires the hydrolysis of cellulose, the main glucose polymer in plants. This catalytic conversion is obtained via a cascade of enzymes (cellulases), capable of depolymerizing cellulose and releasing glucose monomers, which are then fermented by yeasts to produce ethanol.

Among the cocktail of cellulases produced by the fungus *Trichoderma reesei*, one of the key enzyme is the β-glucosidase. This acts at the end of hydrolysis to convert cellobiose, a glucose dimer and the main inhibitor of cellulases. However, this enzyme is produced in limited quantities by *T. reesei* and it is often necessary to supplement it with commercial preparation of β-glucosidases produced by another fungus *(Aspergillus niger).*

To assess the impact of this supplementation with β-glucosidase, a comparison of the two fungal enzymes was necessary. The major difficulty lay in the purification of *T. reesei* β-glucosidase, only representing a few percent of the *T. reesei* cocktail. IFPEN researchers therefore exploited the capacity of the other cellulases to bind to cellulose to eliminate them.

This led to a 95% pure β-glucosidase after a single separation step using FPLC *(Fast Protein Liquid Chromatography).* The development of a microplate activity measurement tool then served to compare the physicochemical properties of the two enzymes using very small quantities.



Comparison of the measured (dots) and predicted (curves) specific activity for T. reesei and A. niger β-glucosidases.

The results demonstrated a thermostability and optimum activity temperature identical for both enzymes. Moreover, it was possible to determined that the *A. niger* enzyme presents a weaker specific activity and a greater sensitivity to glucose. All these data led to validation of a shared kinetic model, now incorporated into a more global biomass enzymatic hydrolysis model.

M. Chauve , ***H. Mathis,*** *D. Huc,* ***D. Casanave, F. Monot, N. Lopes Ferreira.*** Comparative kinetic analysis of two fungal beta-glucosidases. *Biotechnol Biofuels, 2010, 3(1): 3.*

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MOFs trap CO_2 as they breathe

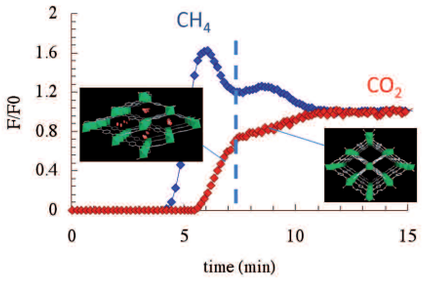
MOFs *(Metal Organic Frameworks)* are good absorbent materials. Some of them are capable of "breathing": they swell above a certain CO_2 pressure, enabling them to adsorb more CO_2. This effect is associated with a change in the crystalline structure, between an open form and a closed form. To exploit this "breathing" in an industrial separation process, it is necessary to determine the behavior of MOFs in the presence of CO_2 mixed with other gases, in particular with methane.

In contrast with conventional adsorbents, the structure of breathing MOFs is modified by adsorption. The structural change in turn modifies the adsorption properties. To understand how this works, IFPEN has, in collaboration with partners from university, developed a methodology to characterize both the adsorbent material and the adsorbed phase.

To explore the interaction between CO_2/CH_4 mixtures and the breathing MOF, an innovative combination of techniques, on several scales, has been designed and implemented by the Lavoisier Institute, the Charles Gerhardt Institute, the Provence Chemical Laboratory and the Caen Catalysis and Spectroscopy Laboratory. In situ spectroscopic methods (DRX and Raman) were used to elucidate the evolution in the structure of the MOF and in the composition of the adsorbed phase as a function of the mixture's composition and pressure. These observations were supplemented by numerical simulations of the adsorption on a molecular scale, as well as separation tests on CO_2/CH_4 mixtures, on a macroscopic scale.

It emerges that the closed form of MOF is highly selective with respect to CO_2, but that its adsorption capacity is low. The reverse is seen for the open form. In addition, a phenomenon of hysteresis occurs, limiting the material's regeneration efficacy.

These results have led to the identification of the factors governing transitions between the closed and open forms of the MOF studied. This detailed understanding of the mechanisms involved paves the way for the design of new breathing MOFs, by producing a robot portrait of the ideal candidate.



Separation of CO_2 and CH_4 by a MOF column (flow rate exiting the column vs. adsorption time). A closed form → open form transition occurs.

L. Hamon, P. Llewellyn, T. Devic, G. Clet, V. Guillerm, ***G. Pirngruber****, G. Maurin, C. Serre, G. Driver, W. Van Beek,* ***E. Jolimaître,*** *A. Vimont, M. Daturi, and G. Férey,* Co-adsorption and separation of CO_2-CH_4 mixtures in the highly flexible MIL-53(Cr) MOF type material. *J. Am. Chem. Soc., 2009, 131, 17490. DOI:10.1021/ja907556q*

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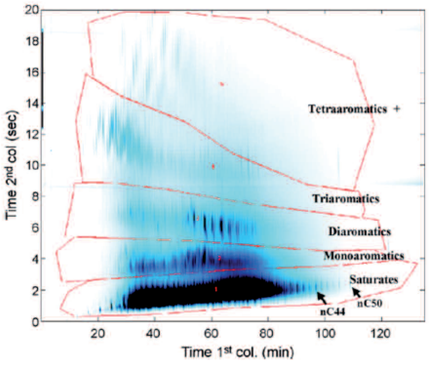
Chromatography's hot!

For the past few years, a growing proportion of heavy compounds in crude oils has been observed. To obtain more diesel fuels that meet requirements from these crudes, the refining industry has developed processes such as hydrotreatment and hydrocracking of vacuum distillates (vacuum distillate corresponds to compounds distilled at temperatures in the range of 350-600°C). In order to optimize these processes and the associated catalysts, efficient feed and effluent characterization methods are required.

Developed in the 1990s, comprehensive two-dimensional gas chromatography (GC×GC) has proved to be particularly efficient for characterizing diesel cuts (between 150 and 350°C), enabling detailed analysis of their components by chemical family and by number of carbon atoms.

Following PhD projects conducted at IFPEN, and working closely with the PECSA laboratory in ESPCI ParisTech, careful selection of columns and separation conditions led to a higher temperature GC×GC analysis method being proposed for the study of heavy cuts, such as vacuum distillates. It has been demonstrated that compounds containing up to 60 carbon atoms and with a boiling point of 615°C could be analyzed using this technique, while separating the components present in vacuum distillates on the basis of their polarity and volatility.



HT-GCxGC chromatogram of a vacuum distillate.

These results have opened up new avenues for the use of high-temperature GC×GC; its application, in combination with pre-separation methods and specific detectors, could lead to better control of vacuum distillate conversion processes, thanks to a better knowledge of their composition.

T. Dutriez, M. Courtiade, D. Thiébaut, H. Dulot, ***F. Bertoncini,*** *J. Vial, M.-C. Hennion, J. Chrom. A, 2009, 2905-2912. DOI :10.1016/j.chroma.2008.11.065*

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Strength in numbers (of investigation methods)

Crude oils contain asphaltenic compounds, causing them to behave in specific ways. Hence, key characteristics underpinning the ease of crude oil production and refining, such as stability and viscosity, depend on how the asphaltenes are organized (aggregation versus dispersion). In particular, this has an impact on transport properties in porous media (underground rocks or catalyst supports), adsorption and wettability phenomena, as well as emulsion or gas hydrate granule stabilization.

The development of oil processes requires a better understanding of how these asphaltenes are organized and how they aggregate in operational conditions. To date, this knowledge has been limited, firstly, by the natural diversity of crudes and, secondly, by the fragmentary nature of the information accessible via each of the investigation methods employed.

In order to build a robust, unified model shared by the oil community to describe the behavior of asphaltenes, IFPEN joined forces with internationally renowned teams to implement a strategy[1] incorporating the observations of each of the laboratories involved, obtained on several products, and the combination of complementary physico-chemical analysis methods. In particular, IFPEN contributed its expertise in the field of radiation scattering and thus helped to specify the different phases in asphaltene aggregation[2].

The descriptive model resulting from this joint project is shown in diagram form in the figure. On a molecular lengthscale, the dominant species include polycondensed aromatic cycles surrounded by alkyl chains. These molecules combine on a scale of a few nanometers to form aggregates of 6 to 10 molecules. On a larger scale, these nano-aggregates themselves form loose, polydispersed clusters.

This multiscale description represents an essential tool to understand and describe the properties of fluids containing asphaltenes.

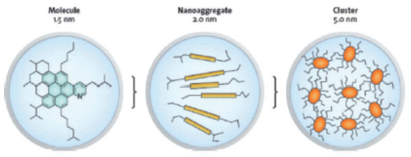

Diagram depicting the hierarchized and multiscale organization of asphaltenes[1].

(1) *O.C. Mullins, H. Sabbah, J. Eyssautier, A. E. Pomerantz,* ***L. Barré,*** *A. B. Andrews, Y. Ruiz-Morales, F. Mostowfi, R. McFarlane, L. Goual, R. Lepkowicz, T. Cooper, J. Orbulescu, R. M. Leblanc, J. Edwards, R. N. Zare,* Advances in Asphaltene Science and the Yen-Mullins Model, *Energy & Fuels, 2012, 26 (7), 3986–4003.*

(2) *J. Eyssautier, P. Levitz,* ***D. Espinat****, J. Jestin, J. Gummel, I. Grillo,* ***L. Barré,*** Insight into Asphaltene Nano-Aggregate Structure Inferred by Small Angle Neutron and X-Ray Scattering, *J. Phys .Chem. B., 2011, 115, 6827–6837.*

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Helping CO_2 and brines to coexist

Interfacial fluid tension (IFT), just like wettability, is a factor known to influence the distribution and circulation of fluids in porous media. Consequently, in the context of geological CO_2 storage in deep saline aquifers, the brine/CO_2 IFT is a crucial factor determining not only the amounts of CO_2 that can be stored, but also the conditions for its injection into the underground environment.

However, data concerning this fluid system, in appropriate pressure and temperature conditions, are sparse, since the measurements required are lengthy and difficult to perform in a reliable and reproducible manner. It is for this reason that IFPEN has adapted pre-existing measurement hardware to the case of CO_2 and developed data interpretation software.

The measurement in question, known as the hanging (or rising) drop method, is based on shape characterization of this drop and makes it possible to determine interfacial tensions at up to 130°C and 350 bar.

In particular, measurements have been made between CO_2 and NaCl brines at variable concentrations, under different pressure and temperature conditions.

The influence of the salt's valency was also studied. While the IFT increases in a linear manner with the molar salt concentration, this increase in IFT is also related to the nature of the salt: it is twice as high with $CaCl_2$ than with NaCl.

In addition, it is observed that the total increase in IFT as a function of brine composition (NaCl + $CaCl_2$) is the sum of the two individual increments. The effect of the salts on the IFT is therefore additive.

These results have been successfully modeled, making interfacial tension a predictable parameter. This study has made it possible to accurately predict for the first time the IFT for each aquifer considered, on the basis of pressure, temperature and concentration in various salts.

CO_2 bubble in brine.

C. Chalbaud, ***M. Robin, J.-M .Lombard, F. Martin,*** *P. Egermann, H. Bertin,* Interfacial tension measurements and wettability evaluation for geological CO_2 storage. *Advances in Water Resources 209, 32, 98–109.*

C.A. Aggelopoulos, M. Robin, O. Vizika, Interfacial tension between CO_2 and brine (NaCl + $CaCl_2$) at elevated pressures and temperatures: The additive effect of different salts. *Advances in Water Resources, 2011, 34, 505–511.*

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Combustion goes fluorescent

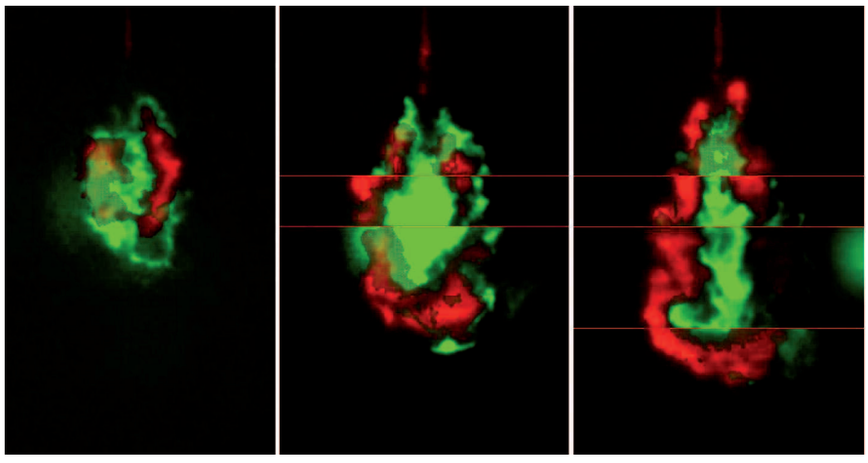
To develop energy-efficient engines and reduce their greenhouse gas emissions, it is necessary to understand the physical phenomena that occur when the fuel is added to the combustion chamber, mixed with air and then burned. To do so requires the availability of detailed information on the parameters controlling combustion: the fuel concentration, the rate at which it is mixed with air, as well as the concentration in other intermediate species involved in combustion.

The methods widely used to obtain this type of information are based on the fluorescence of molecules excited by a laser sheet. They do not modify the medium in which the measurements are taken and provide two-dimensional information (particularly concentration ranges) as well as quantitative information.

IFPEN has been developing techniques of this kind for a number of years in order to overcome the difficulties related to the combustion chamber environment: reduced optical accessibility, high pressure and high temperature gradients, etc. As a result, it now boasts equipment and expertise that are extremely rare in this field.

In particular, significant advances have been made in the characterization of the various intermediate species formed during combustion. The results yielded for diesel combustion — a complex process — enable a better understanding of the physical phenomenon involved.

Developments are continuing with the aim of performing increasingly quantitative and precise measurements and extending their scope to other parameters of interest (other reactive species, soot particles, temperature in the reaction zone, etc.).



Evolution in the structure of combustion of a diesel jet by laser-induced fluorescence: in green the low temperature (periphery) and fuel-rich (center) zones and in red the high temperature zones.

G. Bruneaux, *International Journal of Engine Research, 2008, (9)3.*

R. Devillers, ***G. Bruneaux,*** C. Schulz, *Appl. Phys., 2009, 96, 735-739.*

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Scientific visitors

• **Professor Camilla Gambini Pereira** *from the Federal University of Rio Grande do Norte (Brazil) was hosted at IFPEN for a period of one year. Her work focused on modeling the phase equilibria of mixtures containing oxygen compounds, hydrocarbons and gas compounds.*

• **Gergina Pencheva**, *research assistant in the CSM at the University of Texas, has been hosted by the Technology, Computer Science and Applied Mathematics Division since March 2014. Her work focuses on digital modeling in the field of geosciences and, in particular, multiscale methods and a posteriori error estimators.*

Upcoming scientific events

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– Photocatalysis for Energy –*** *15-17 October 2014, IFPEN-Lyon - www.rs-photo4e.com.*

• *IFP Energies nouvelles' "Rencontres scientifiques" event* ***– LES for ICE –*** *4-5 December 2014, IFPEN Rueil-Malmaison - www.rs-les4ice.com*

Innovation

In 2013, IFPEN was in 13th position in the INPI (French National Industrial Property Institute) rankings of patent filers. With 188 applications, IFPEN is among the top three research bodies in France, with the French Atomic Energy Commission (CEA), and the French National Scientific Research Center (CNRS). When adjusted to account for workforce, IFPEN climbs to number one. Almost half of these patents concern new energy technologies.

Managing Editor: Marco De Michelis
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ISSN No. 1957-3537

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