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Molecular characterization of liquid and gas systems, assay of species in ultra-trace conditions, representation of nano-organized complex fluids on different scales, description of material textures from the nanometric to the millimetric scale, characterization of systems in representative operating conditions: the Physics and Analysis Division is focusing on all these issues, and more, to support IFPEN's innovation projects.

Its researchers work to develop cutting-edge methods and techniques, particularly as part of pivotal academic partnerships.

Their nationally and internationally recognized expertise covers an exceptionally broad spectrum of matter states, giving them access to detailed physicochemical descriptions and the properties of numerous systems of interest. They make a major contribution to IFPEN's scientific influence, with more than 20 papers published every year in high-impact journals. This issue presents just a few of these papers.

I hope you enjoy reading it.

Cécile Barrère-Tricca,
Head of the Physics and Analysis Division

Mercury in refineries plummets

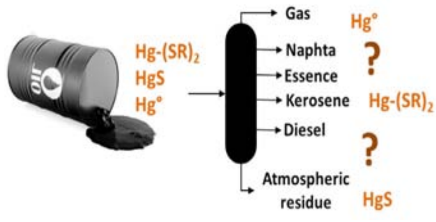
Reducing mercury emissions related to industrial activities is an important issue for today's society. Although oil crudes only contain very low concentrations (from a few µg/l to a few dozen mg/l in liquids, and up to a few µg/m³ in gases), the refining industry needs to tackle this problem due to the potential harmful effects of mercury – even at low doses – on operator health and industrial equipment (corrosion).

Mercury can be removed from oil fluids by making it react on dedicated solids, which absorb it irreversibly (adsorbents). However, the effectiveness of this treatment depends on the chemical forms of the mercury present: identifying these forms (speciation) is therefore essential in order to choose the most appropriate elimination solution.

A new speciation protocol has been developed by IFPEN[1] and trialled during a test run in a refinery. This test run demonstrated, firstly, how quickly species change over time; it also led to better characterization of mercury distribution within the various distillation cuts (cf. figure).

In addition, strong interactions between mercury and sulfur (also present in crudes) have been demonstrated on samples taken on-site, using separation methods employing ICP/MS[a] as the elementary detection system.

All these results made it possible to specify the temperature stability ranges of the various chemical forms of mercury, leading to the development of a new thermolysis-based treatment[2].



Mercury and refining: from barrel to distillation column.

a - Inductively Coupled Plasma Mass Spectrometry

(1) ***F. Gaulier, A. Gibert,*** *D. Walls, M. Langford, S. Baker,* ***A. Baudot, F. Porcheron, C.-P. Lienemann,*** *Fuel Processing Technology, 2015, 131, 254-61. DOI: 10.1016/j.fuproc.2014.10.024*

(2) ***F. Guillou, A. Baudot, C.-P. Lienemann, A. Hugon, K. Barthelet, F. Porcheron,*** Procédé d'élimination de mercure d'une charge en aval d'une unité de fractionnement, *brevet déposé sous le n°7123/00/FR-NP.*

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Biobased pyrolysis oils: separating into fractions to more accurately decipher their composition

The thermochemical conversion of lignocellulosic biomass for the production of biofuels or bioproducts requires the development of efficient processes and catalysts. However, to develop these, we need to be able to accurately determine the composition of the conversion products.

This is the case, for example, with oils obtained by fast pyrolysis (a biomass liquefaction process), which present physicochemical properties far removed from those of products derived from fossil fuels: the very broad diversity of chemical structures present (sugars, carbonyls, carboxyls, phenols, etc.), combined with their often highly dispersed molecular weights, pose scientific and technical challenges in terms of their analytical description.

To determine the chemical composition of these oils in as much detail as possible, IFPEN has developed a multi-technique analytical approach.

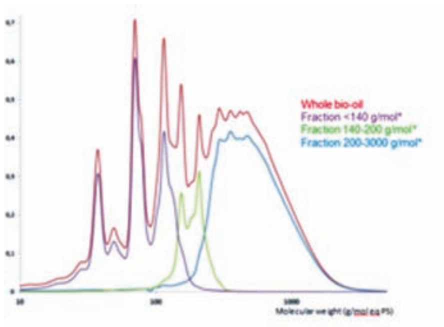
The core analysis is based on chromatography techniques, these being particularly well suited to the compounds present[1], which can be heat-sensitive and have a high polarity and/or molecular weight.

The development of a prior pyrolysis oil fractionation step has led to the physical recovery of different fractions:

- either as a function of the molecular weight of its components, by Steric Exclusion Chromatography (SEC)[2],
- or on the basis of their polarity, by High-Performance Thin-Layer Chromatography (HPTLC).

The next step would be to develop and implement expert after-treatment of the data derived from the various detection devices[a].

a - For example: UV spectroscopy and mass spectrometry



Molecular weight distribution of three fractions collected by fractionation of a rapid pyrolysis oil by SEC.

(1) ***A. Le Masle***, *D. Angot*, ***C. Gouin***, *A. D'Attoma*, ***J. Ponthus, A. Quignard***, *S. Heinisch, Journal of Chromatography A, 2014, 1340, 90-98.*

(2) ***A. Le Masle, S. Sivault, N. Charon, L. Chahen***, publication submitted *in Fuel*, under review.

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MRI: for good impregnation in live conditions

Hydrotreatment processes, which allow to produce low sulfur content fuels, are carried out using heterogeneous catalysts, composed of an active phase – metal sulfides – supported on mesoporous oxydes. The active phase properties – frequently obtained by impregnation of metal salts on these supports – have a significant impact on the catalytic performances.

The impregnation step involves a complex and dynamic combination of phenomena, coupling a process of diffusion in porous media and the interaction of metal ions with the support surface (adsorption). Detailed description of these mechanisms requires *in situ* monitoring – in terms of time and space resolution – of metal species inside the porous volume.

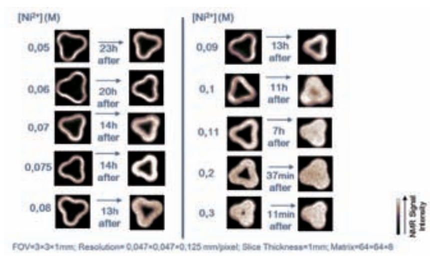
Magnetic Resonance Imaging (MRI) is a method widely used in the fields of chemistry and medicine. Similar to its use in medical imaging, IFPEN has worked with LCMCP[a] to develop an MRI method that uses metal ions as contrast agents.

Hence an MRI image acquisition method has been developed to monitor this catalyst support impregnation step. Finally, innovative tools, developed in-house to process these images, have been used.

Thanks to this research, IFPEN now has access to a powerful tool enabling 3D, time-resolved visualization of the diffusion and chemical nature of metal species inside the catalytic materials under development.

This methodological development will make a significant contribution in terms of optimizing the preparation of future metal/support heterogeneous catalysts.

a - *Laboratoire de chimie de la matière condensée de Paris* - Paris Laboratory for Condensed Matter Chemistry



Evolution of distribution of Ni^{2+} ions inside an extruded alumina support, as a function of time and concentration.

A. Nowacka, J. Moughames, Z. Adem, ***A.-A. Quoineaud, M. Rolland,*** *F. Guenneau, A. Gédéon, Applied Catalysis A: General 2015, 503, 111–116.*

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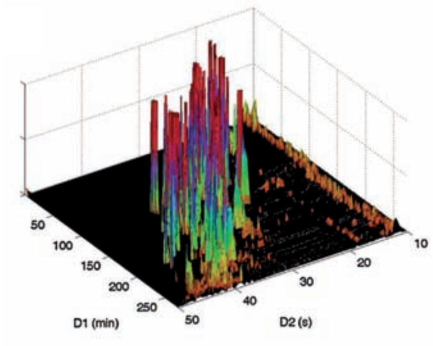
Liquid chromatography takes on a new dimension

To improve the thermochemical or biological biomass conversion processes used in the production of 2nd-generation biofuels, detailed characterization of the products generated at the different stages is essential. However, these products – present within an aqueous matrix – contain a broad variety of chemical species, primarily oxygenated.

To respond to the complexity of these mixtures, analytical tools based on separation techniques have been used, such as liquid chromatography, which is well suited to the analysis of polar, heat-sensitive compounds with high molecular masses.

However, a single separation dimension has been shown to be inadequate to achieve the separation power required to characterize this type of sample. This realization led IFPEN to develop an online two-dimensional version of the technique, based on the following principle: at the end of the first separation step, all the products separated according to a first dimension are sent for a second separation step[1].

The project concerned two-dimensional liquid chromatography equipment with UV detection (LCxLC-UV). It consisted of the selection and dimensioning of separation systems (columns), as well as the definition of optimum analysis conditions (temperature, sampling frequency, elution gradient slope). It led to the development of an operating methodology that maximizes the total capacity of detection peaks for the analysis of real samples.



LCxLC-UV analysis of an aqueous biomass sample: 3D representation.

To improve the analysis quality, based on comparison with the UV signature of model molecules, mass spectrometry detection will soon be introduced, enabling direct identification and quantification of the compounds detected.

(1) ***A. Le Masle,*** *D. Angot,* ***C. Gouin,*** *A. D'Attoma,* ***J. Ponthus, A. Quignard,*** *S. Heinisch, J. of Chromatography A, 2014,1340, 90-98. DOI: 10.1016 / j.chroma.2014.03.020*

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A voyage through a porous nanometric network

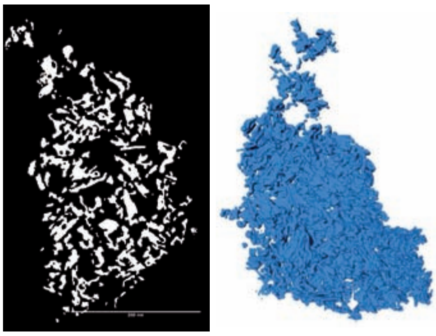
Issues linked to air quality make it necessary to reduce the sulfur content of fuels, achieved using the crude oil hydrotreatment process. One way to improve this catalytic process is to improve the transport of the oil feed through the catalyst granules.

It is therefore important to understand and model the phenomena governing this transport in order to develop more efficient catalysts. To achieve this, it is necessary to have pertinent descriptors related to the porous texture of their supports, from nanometric to granule scale.

Electron tomography is a technique that produces a nanometer-scale reconstruction of the volume of a sample based on a series of 2D images[1]. It is particularly suitable for the 3D visualization of a nanoporous network.

Recent developments achieved by IFPEN have led to a data processing method enabling quantitative texture analysis on a highly local scale. To test its performance, this enriched method was applied to a series of four mesoporous aluminas (catalyst supports) with different textures. In addition to visualizing the arrangement of the alumina platelets forming the mesoporous network (cf. figure), it supplied, after image processing, a measure of the tortuosity and size of the pores at a nanometric scale.

By supplementing macroscopic texture characterization methods, this new tool paves the way for multiscale description of transport properties. When applied to these same supports, but following the addition of the active phase, it will make it possible to study the final porosity of the catalyst grains.



Visualization of the alumina platelets arrangement in a mesoporous support, at a nanometric scale.

(1) ***L. Neveux, D. Chiche, J. Perez-Pellitero,*** *L. Favergeon,* ***A.-S. Gay,*** *M. Pijolat, Phys. Chem. Chem. Phys., 2013, 15, 1532.*

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CT scanning of foam injection in fractured cores

Around 60% of the world's oil reserves are contained in oil fields with a high proportion of carbonate reservoirs, which are fractured and oil wet. These unfavorable properties lead to low oil recovery rates and even injecting water may be ineffective due to the capillary forces that hold the oil inside the porous matrix. In addition, it does not trigger a sufficiently high pressure drop in the fracture to force imbibition in this matrix.

Other recovery processes must, therefore, be considered, in particular, chemical EOR[a]. Laboratory experiments are required to assess their impact on the recovery rate and understand the associated physical mechanisms. These are performed on cylindrical rock samples (cores) with a diameter of 4 cm and a length of 6 cm.

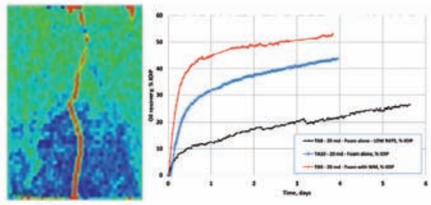
X-ray tomography (CT scanning), enabling 3D real-time monitoring of multiphase flows at the core scale, was used to follow the efficiency of different processes in artificially fractured cores.

Pivotal to the success of the method are: the capacity to clearly differentiate between the contributions of the fracture and the matrix blocks or to show gravity effects; the acquisition speed (up to 6 linear cm/s) enabling the use of "dual energy[b]" mode to simultaneously quantify the 3 fluid phases: water, oil and gas.

The following were therefore studied[1]:

- the injection of foam into the fracture in order to create a pressure gradient to force the oil out of the matrix blocks,
- the addition of a wettability agent to the foam to restore the motor capillary forces, by inverting the wettability of the rock.

In addition to visualization of the phenomena, X-ray tomography provides access to important data for the simulation of enhanced oil recovery processes.



Flow visualization during foam injection in a fractured core and oil recovery curves for 3 different processes.

a - Enhanced Oil Recovery
b - Using the fact that dual-energy X-ray attenuations depend differently on density and atomic number

(1) ***E. Rosenberg, M. Robin, B. Bourbiaux, S. Gautier,*** *M. Chabert, E. Chevallier, SPE-179811-MS Oman 2016 Conference CT-scan monitoring of combined chemical EOR processes in fractured carbonate cores.*

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News

• The 2nd session of IFP School's MOOC dedicated to "Sustainable mobility: technical and environmental challenges for the automotive sector", on-line from 2 November to 7 December 2015, was a great success: more than 5,200 people signed up, with 32% of these completing the whole course and 92% recommending it!

• A second session of the "Oil and Gas: from exploration to distribution" MOOC was launched on 14 March.

Awards

*• **Fadi Henri Nader** received the "Distinguished Service Award" from the Middle-East section of the American Association of Petroleum Geologists (AAPG) for his commitment and efforts to promote geosciences in the Middle-East (6 March 2016).*

Upcoming scientific events

*• IFP Energies nouvelles' "Rencontres scientifiques" event **DEFI: Dynamics of Evolving Fluid Interfaces – Gathering physico-chemical and flow properties –** 12-13 October 2016, IFPEN-Lyon – www.rs-defi2016.com*

*• IFP Energies nouvelles' "Rencontres scientifiques" event **LES4ICE 2016 : Large-Eddy Simulation for Internal Combustion Engine Flows –** 30 November and 1st December 2016, IFPEN Rueil-Malmaison www.rs-les4ice.com*

Publications

• OGST – IFP Energies nouvelles journal – Issue 1, volume 71 (2016). Issue dedicated to the LES4ICE 2014 Scientific event.

• OGST – IFP Energies nouvelles journal – Issue 2, volume 71 (2016). Tribute to Yves Chauvin.

http://ogst.ifpenergiesnouvelles.fr

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IFP Energies nouvelles

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