Science@ifpen

Issue 39 - December 2019

SPECIAL ISSUE
Recent PhD graduates

The 2019 Yves Chauvin Prize was awarded to Céline Pagis for her thesis conducted under the aegis of the Catalysis, Biocatalysis and Separation Division and supervised by IRCELYON[a], which led to the development of materials suitable for a variety of applications in the energy and agrifood sectors.

This thesis is emblematic of a long-standing expertise of IFPEN (catalysis for oil refining), which now makes it possible to address themes such as the biomass conversion or photocatalysis for CO_2 valorization.

As is the case for all candidates for the Prize, this work is also the result of open science and excellence policy, initiated several years ago and supported by the Scientific Board, providing a launch ramp to prepare technological innovations for the energy transition: openness towards outside academic and industrial partners, excellence of IFPEN's researchers singled out for numerous awards.

I have been delighted to be part of this pivotal strategic approach aimed at ensuring IFPEN continues to play a leading role within the research and innovation community.

I hope you enjoy reading this issue.

Pierre-Henri Bigeard,
Former Executive Vice-President Research and Innovation of IFPEN

a - Institute of Research on Catalysis and Environment of Lyon.

Faujasite zeolite: a new generation is born

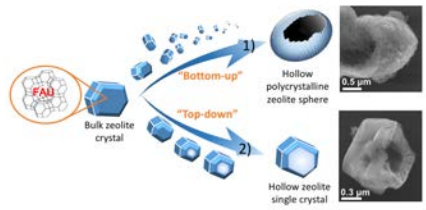
Thesis by Céline Pagis, 2019 Yves Chauvin prize*

Zeolites, inorganic crystallized materials containing nanometric pores and channels, are capable of trapping various chemical substances or catalyzing numerous reactions. These distinctive properties make them ideal materials for a large number of industrial processes. However, during chemical reactions, the nanometric size of the channels (< 2 nm) limits molecule diffusion, affecting reaction speeds and reducing the useful fraction of each crystal. To counter this phenomenon, generating additional porosity amounts to creating "highways", thereby improving molecule flow.

This PhD thesis was conducted using faujasite zeolite (FAU) to explore synthesis routes leading to a new architecture, and more precisely to produce a zeolite in which the crystals, named "nanoboxes", have a single internal cavity[1], with some major associated advantages:

- crystal size and structure maintained,
- nanometric dimensions of the wall making it possible to improve molecule diffusion within the crystal,
- creation of a favored molecule storage zone.

Two synthesis methods were developed (figure): the 1st consists in agglomerating zeolite nanocrystals to form hollow capsules, and the 2nd in preferentially dissolving the center of each crystal, thereby creating the internal cavity. Following the evaluation of the diffusional and catalytic properties of these new materials, a beneficial effect in terms of reduction in their characteristic diffusion length was demonstrated on their activity and their catalytic efficiency[2].



The two synthesis routes developed making it possible to obtain hollow FAU zeolite crystals.

This new approach paves the way for a greater understanding of the impact of structural zeolite parameters on molecule diffusion within them, with a view to improving this phenomenon.

*Thesis entitled **"Synthesis and catalytic evaluation of hollow zeolite Y crystals"**

(1) **C. Pagis**, A. R. Prates, D. Farrusseng, **N. Bats**, A. Tuel, Chem. Mater. 28 (2016) 5205-5223
DOI: 10.1021/acs.chemmater.6b02172

(2) **C. Pagis**, F. Meunier, Y. Schuurman, A. Tuel, **M. Dodin**, **R. Martinez Franco**, D. Farrusseng, ChemCatChem 10 (2018) 4525-4529
DOI: 10.1002/cctc.201801225

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Ebullated bed reactors: paths and wakes hit the headlines!

Thesis by Clément Toupoint*

Ebullated bed chemical reactors are widely employed in the chemical engineering and petrochemical sectors. However, the hydrodynamics of ebullated bed reactors containing catalytic particles are poorly understood, often leading to units of this type being oversized.

It is quite natural given the complexity of the physical phenomena at play that the various problems should be subdivided into more targeted subjects. Accordingly, this thesis was dedicated to the local hydrodynamic mechanisms of isolated cylindrical particles, the first essential step prior to moving onto the study of the numerous interactions between particles in an industrial ebullated bed.

Initial research focused on the anisotropy effects of an isolated cylindrical catalyst grain on its free fall in a liquid (figure). The regimes observed were classified, on the basis of adimensional parameters such as density and elongation ratios and the Archimedes number[a]. Three free fall path modes were thus identified.

Next, as part of an initial approximation of the confinement effects[b], the free fall of cylindrical particles in 2D confined media (Hele-Shaw cell[c]) was studied with or without the presence of a swarm of ascending bubbles. High speed camera and advanced processing techniques made it possible to determine and analyze in detail the correlation between the changes in the paths of the free-falling particles and their interactions with ascending bubbles[1].

Extending the kinematic models resulting from this research to a larger number of particles will give rise to predictive Euler-Euler models that will be used to design future industrial installations. This research will be continued as part of a collaborative program[d].

(1) ***C. Toupoint,*** *P. Ern, V. Roig, Journal of Fluid Mechanics, 2019, Vol. 866, pp. 82-111, https://doi.org/10.1017/jfm.2019.77*

a - Relationship between buoyancy and viscous effects.
b - Due to the large number of particles in a real ebullated bed.
c - Experimental apparatus composed of two glass plates placed very close together.
d - ANR MUSCATS project, with the Toulouse Institute of Fluid Mechanics and the Toulouse Chemical Engineering Laboratory.

*Thesis entitled ***"Path and wake of cylinders falling in a liquid at rest or in a bubble swarm - towards the hydrodynamic modeling of ebullated bed reactors"***

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Bubble fineness: the secret of successful reactions

Thesis by Luca Gemello*

Bubble flows are widely used in the chemical and biotech industries, since they are an easy way to introduce gas reactants into a liquid medium. In all these industrial cases, knowing the bubble size is essential to the dimensioning of reactors since it is this that governs hydrodynamics and transfer of reactants.

Predicting the size and distribution of bubbles in reactors and fermenters is traditionally based on empirical correlations that, by nature, cannot be transposed from one geometry or system to another.

To overcome this, a multi-physical and multi-scale modeling approach was developped, incorporating physical bubble breakup and coalescence models into a population balance modeling. The combined use of CFD[a] and a QMOM[b] method, results in reduced calculation times[1], a major issue in the industrial context.

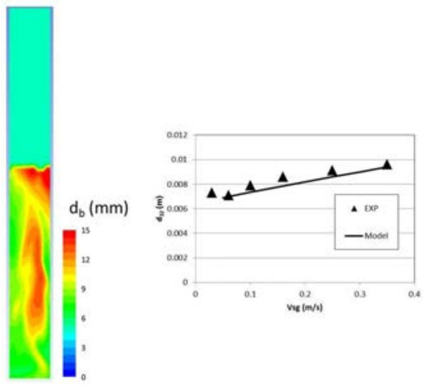
The complete model was validated on a variety of flow geometries and operating conditions[2]. It represents a major advance for the prediction of bubble size in large-capacity industrial reactors and fermenters.

It is currently being extended to non-Newtonian rheology systems, such as fermentation broth, involved in biofuel production.

a - Computational Fluid Dynamics.
b - Quadrature Method Of Moments.

(1) ***L. Gemello, V. Cappello, F. Augier,*** *D. Marchisio,* ***C. Plais,*** *Chemical Engineering Research and Design, 2018, 136, 846-858. https://doi.org/10.1016/j.cherd.2018.06.026*

(2) ***L. Gemello, C. Plais, F. Augier,*** *D. Marchisio, Chemical Engineering Journal, 372, 2019, 590-604. https://doi.org/10.1016/j.cej.2019.04.109*



Prediction via the calculation of bubble diameters and comparison with experimental data (Ø 400 mm bubble columns, water-air system).

*Thesis entitled **"Hydrodynamic modeling of bubble columns using an approach combining two-fluid models and a population assessment"**

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An explosive cocktail for steel fracture?

*Thesis by Martien Duvall Deffo Ayagou**

Hydrogen sulfide (H_2S) is a toxic gas found both in nature (green algae fermentation) and the industrial environment[a]. On contact with water, it forms an acid solution liable to cause steel corrosion via the oxidation of iron, with the formation of a deposit that acts as a protective barrier to varying degrees and the generation of hydrogen gas on the metal surface. H_2S then facilitates the mass penetration of hydrogen into the steel, causing internal damage leading to fracture and, ultimately, structural failure.

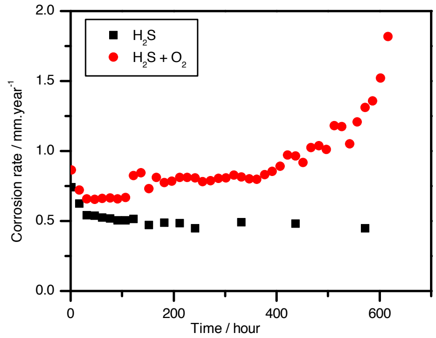
Well documented in the oil sector, in which environments tend to be devoid of oxygen, this problem has not been studied in the biomass and geothermal sectors, with environments that can contain both H_2S and air. It was therefore important to verify to what extent reactions between H_2S and O_2 affect steel corrosion and weakening by hydrogen.

The research carried out highlighted the main products of the reaction between H_2S and O_2 dissolved in aqueous medium, sulfates and sulfites, resulting in acidification of this medium[b(1)]. In addition, the iron sulfide deposit that forms on the surface of the steel is less dense and less protective in the presence of O_2. These modifications lead to a considerable increase in the speed of corrosion (figure). In addition, the concentration of hydrogen in the steel is much greater in the presence of air[(2,3)].

These results suggest that serious corrosion problems and increased weakening risks due to hydrogen are likely with the simultaneous presence of H_2S and O_2. For the new energy sector, where just such an environment may exist, these risks will have to be taken into account when selecting metals.

a - In natural gas or biogas, for example.
b - Fall of close to one unit of pH per month in the presence of O_2.

*Thesis entitled **"Impact of oxygen and H_2S on the corrosion of pure iron and on hydrogen concentration"**



Variations in the speed of steel corrosion in aqueous media containing dissolved H_2S, in the absence or presence of oxygen.

(1) ***M. D. Deffo Ayagou, G. R. Joshi,*** *T. T. Mai Tran, E. Sutter, B. Tribollet, C. Mendibide, C. Duret-Thual,* ***N. Ferrando, J. Kittel,*** *Corrosion 75, 4 (2019), p. 389–397. DOI: 10.5006/3092*

(2) ***M. D. Deffo Ayagou,*** *T. T. Mai Tran, B. Tribollet,* ***J. Kittel,*** *E. Sutter,* ***N. Ferrando,*** *C. Mendibide, C. Duret-Thual, Electrochimica Acta 282 (2018), p. 775–783. DOI: 10.1016/j.electacta.2018.06.052*

(3) ***M. D. Deffo Ayagou, J. Kittel,*** *C. Mendibide, C. Duret-Thual,* ***K. Belkhadiri,*** *T. T. Mai Tran, E. Sutter, B. Tribollet,* ***N. Ferrando,*** *Corrosion 74, 11 (2018), p. 1192–1202. DOI: 10.5006/2893*

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Lasers and algorithms to limit soot

*Thesis by Fabien Tagliante**

The distance between the fuel injector and the location where the flame stabilizes[a] is a major factor affecting soot production in the chambers of compression ignition engines. This production is reduced or even eliminated when the distance in question is sufficiently large.

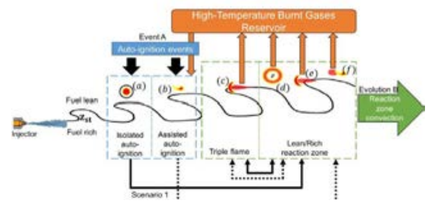
This distance is governed by the interactions between the turbulent flow, generated by the very high-pressure liquid fuel jet, and the reactions resulting from the ensuing chemical kinetics. In order to be understood, these complex interactions need to be studied on very small scales and under severe thermodynamic conditions.

This was done through the combined use of optical diagnostics and numerical simulations. For the experimental research, a high-pressure chamber was used, with optical accesses to enable the evolution of the jet and its combustion to be visualized over time using various simultaneous laser techniques[(1)]. 3D simulations of gas jets similar to real two-phase liquid/gas flows were conducted, providing a highly detailed reproduction of local interactions[(2)].

The resulting conceptual model (figure) provides a more accurate understanding of the interactions between the phenomena identified in previous research – the counter-current propagation of premixed flames and auto-ignitions (spontaneous or under the effect of hot gases) – and, for the first time, a detailed understanding of their impact on diesel flame stabilization.

Simplified modeling approaches using new knowledge may lead to the development of technical solutions to significantly reduce soot produced in compression ignition engines.

*Thesis entitled ***"Combined study by direct numerical simulation and optical diagnostics of the flame stabilization in a Diesel spray"***



Conceptual model for diesel flame stabilization.

(1) ***F. Tagliante, L. M. Malbec, G. Bruneaux,*** *L. M. Pickett,* ***C. Angelberger.*** *DOI: https://doi.org/10.1016/j.combustflame.2018.07.024*

(2) ***F. Tagliante,*** *T. Poinsot, L. M. Pickett, P. Pepiot,* ***L. M. Malbec, G. Bruneaux, C. Angelberger.*** *DOI: https://doi.org/10.1016/j.combustflame.2018.12.007*

a - So-called lift-off distance.

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Interactions between clay minerals and anionic surfactants

Thesis by Ariane Suzzoni*

The interaction between surfactants and clay minerals is a well-known source of problems in the field of enhanced oil recovery[a] since it can induce a modification in the injected formulations and a decrease in productivity due to pore plugging. This phenomenon also concerns the pollution remediation sector, in both land and water environments. The aim of the research conducted for this thesis was to gain a better understanding of the mechanisms at play.

Initially, the interaction mechanisms were studied via tests involving the aqueous phase adsorption of anionic surfactants on the surface of mineral clays (kaolinite and illite), which are simultaneously representative and very different from one another[b] (1). The influence of surfactant concentration on aqueous suspension stability was then studied via a combination of sedimentation monitoring over time, rheological measurements and small angle X-ray scattering (SAXS) experiments[c].

For kaolinite, these measurements revealed a dispersion of the particles in the presence of surfactants. Analysis of the microscopic structure of suspensions using SAXS reveals a strong correlation between surfactant concentration and the orientation of individual particles within sediments (figure), with consequences for petrophysical and confinement properties.

Such behavior was not observed with illite suspensions, in which there was little particle orientation within sediments. Beyond the observations made, combining the data acquired relating to these colloidal dispersions made it possible, for the first time, to link their macroscopic behavior to adsorption, wettability and particle orientation properties.

This experimental work is therefore a first stage that has provided a raft of useful information for effluent treatment, separation by flotation and any other process involving flows in porous media.

The effect of anionic surfactants on clay particles.

a - Or EOR.
b - Particles of these clays differ in terms of their size, shape factors and the charges they carry.
c - Particularly at SOLEIL Synchrotron.

(1) ***A. Suzzoni, L. Barre, E. Kohler,*** *P. Levitz, L. J. Michot,* ***J. M'Hamdi,*** *Colloids and Surfaces A: Physicochemical and Engineering Aspects, volume 556, nov. 2018. DOI: 10.1016/j.colsurfa.2018.07.049.*

*Thesis entitled **"Evolution of the structure of clay minerals during their interactions with anionic surfactants"**

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Operando spectroscopy in all transparency

Thesis by Marisa de Sousa Duarte*

Article published in issue 36 of Science@ifpen, march 2019

*Thesis entitled **"Measure, inside a reactor, of spatial and temporal profiles of liquid and solid phases by spectroscopic analyzes"**

News

• ***Launch of the Carmen joint research laboratory*** *focusing on materials characterization for new energies by IFPEN, the CNRS, Sorbonne University, Strasbourg University, ENS Lyon and Claude Bernard Lyon 1 University.*

Scientific visitor

• ***Vania Santos-Moreau,*** *from the Process Design and Modeling Division, visiting professor at University College London for three years.*

Award

• ***Benoît Noetinger,*** *from the Geosciences Division, received the Rheims Foundation's Adrien Constantin de Magny Prize at the annual awards ceremony of the French Academy of Sciences.*

Upcoming scientific event

• ***31st European Symposium on Applied Thermodynamics ESAT 2020*** *– 28 June to 1 July 2020 – Paris – www.esat2020.com, co-organized with Mines ParisTech.*

Appointments

• ***Éric Heintzé,*** *IFPEN's Scientific Director, has been appointed member of the Scientific Board at ENS Lyon, for a second five-year term.*

• ***Fadi Henri Nader*** *from the Energy Resources Business Unit has been appointed holder of the "Multiscale fluid-rock interactions" chair at Utrecht University for a period of five years.*

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Managing Director: Jean-Christophe Flèche
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Graphic Design: Esquif
ISSN No. 1957-3537

IFP Energies nouvelles