Science@ifpen
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SPECIAL ISSUE
Recent PhD graduates

For IFPEN, a major research and training player, hosting PhD students is an essential mission. These young emerging researchers contribute their dynamism, their fresh vision and their expertise to our fundamental research. In return, they benefit from a high-quality environment and have access to actual challenges and problems that prepare them for their future careers.

Our PhD students also play a central role in our partnerships with French and international academia. These partnerships are essential in order to overcome the scientific challenges inherent to the development of our innovations and to compare our research with that of the best teams. Moreover, our PhD students regularly win awards reflecting the quality of their work.

Scientific excellence and high standards must be maintained and recognized, and it is the purpose of the Yves Chauvin prize. Every year, several PhD students selected by their respective research divisions compete to win it.

In this issue, you can read about the thesis subjects submitted for selection to the Scientific Committee, and in particular those of the two joint laureates: Rémi Hocq and Jérôme Rey.

I hope you enjoy reading this issue,

Pierre-Franck Chevet,
IFP Energies nouvelles' Chairman and CEO

Optimization of a microorganism of interest for the bioproduction of isopropanol and n-butanol

Thesis by Rémi Hocq, 2020 Yves Chauvin prize-winner*

A major challenge of the energy transition, the substitution of petrochemical processes by bioprocesses requires the use of catalysts (or microorganisms) to produce molecules for industry, with a lower impact on the environment. One of these microorganisms, *Clostridium beijerinckii* DSM 6423, is capable of converting a broad variety of sugars into n-butanol and isopropanol — bio-alcohols that can be used directly or dehydrated to produce propylene and butenes — *via* fermentation. However, its fermentation performances are currently too low, limiting its use on an industrial scale.

This thesis project (figure) focused firstly on fermentation performances in the presence of sugar industry by-products (molasses). This work consisted in stabilizing physiological states in continuous culture conditions, then characterizing them *via* an *in silico*[a] approach. Thereafter, the combined use of the latest omic analysis tools[b], probing *C. beijerinckii* DNA, RNA and proteins, generated fundamental data shedding light on its metabolism and establishing a robust and crucial working platform for its ultimate exploitation. Finally, in order to optimize the microorganism's capacities, a major challenge was overcome with the design of a first genetic modification tool[c] and its use to characterize the sigma 54 protein, an essential factor for the production of alcohol in this microorganism[1-2].

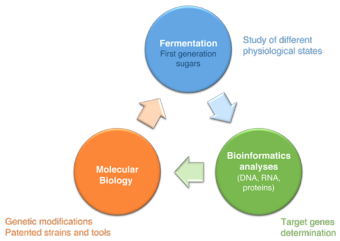


Diagram of the approach adopted.

Hence, *via* the creation and intellectual protection of a first "platform" strain, this same tool has paved the way for the optimization of the fermentation performances of this microorganism of industrial interest.

a - Using complex computer-based calculations or computer models
b - Molecular scale analyses of DNA (genomic), RNA (transcriptomic) and proteins (proteomic)
c - Based on CRISPR-Cas9 technology

*Thesis entitled **"Clostridium beijerinckii *DSM 6423, an emerging platform strain for solvent bioproduction*"**

(1) ***R. Hocq, M. Bouilloux-Lafont, N. Lopes Ferreira, F. Wasels.*** *Sci Rep. 2019; 9(1):7228. DOI: 10.1038/s41598-019-43822-2*

(2) *M. Diallo,* ***R. Hocq,*** *F. Collasa,* ***G. Chartier, F. Wasels,*** *H. Surya Wijayaa, M.W.T. Werte, E.J.H. Wolberta, S.W.M.Kengen, J. der Oost,* ***N. Lopes Ferreira,*** *A.M. López-Contreras. Methods. 2020; 172:51-60. DOI: 10.1016/j.ymeth.2019.07.022*

Scientific contact:
francois.wasels@ifpen.fr

Pretreatment and deformulation of biomass-based products

Thesis by Alexis Dubuis*

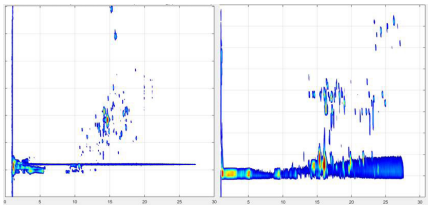
The development of production processes for fuel and platform molecules[a] from lignocellulosic biomass requires knowledge of the chemical composition, on a molecular scale, of the various liquid products generated. But the complexity of the latter makes it necessary to incorporate a "deformulation" step upstream of the actual analysis, without causing any loss or modification of the compounds present.

This thesis research related to two original fractionation methods based, on the one hand, on solubility, with liquid-liquid extraction (LLE) techniques and centrifugal partition chromatography (CPC) and, on the other hand, molecular size with steric exclusion chromatography (SEC). LLE and CPC are used for the selective extraction of sugars, neutral compounds (furans, aldehydes, ketones, alcohols, esters), carboxylic acids and phenols[1-2] while SEC is used for a more specific sugar separation[3]. The actual analysis was then conducted on each fraction obtained, *via* reversed-phase liquid chromatography, with ultraviolet and mass spectrometry detection (RPLC-UV/MS).

The pretreatment and deformulation steps not only enable a simplification of the samples to be analyzed but also structuring on the basis of the properties of the chromatograms generated, thereby facilitating their exploitation. The innovative 2D maps generated contain an abundance of information on the chemical composition of the bioproducts (figure). For an even more detailed characterization, this methodology could be combined with chemometric data analysis.

a - Molecules used as a building block in numerous applications

*Thesis entitled ***"Deformulation of complex biomass-based matrices and characterization via liquid phase chromatography combined with mass spectrometry"***



SECxRPLC/MS (left) and CPCxRPLC/MS (right) maps obtained for a product derived from the biochemical conversion of wheat straw.

(1) ***C. Reymond, A. Dubuis, A. Le Masle, C. Colas, L. Chahen,*** *E. Destandau,* ***N. Charon,*** *Journal of Chromatography A (2020), 1610. https://doi.org/10.1016/j.chroma.2019.460569*

(2) ***A. Dubuis, A. Le Masle, L. Chahen,*** *E. Destandau,* ***N. Charon.*** *Journal of Chromatography A (2019) 1597. https://doi.org/10.1016/j.chroma.2019.03.031*

(3) ***A. Dubuis, A. Le Masle, L. Chahen,*** *E. Destandau,* ***N. Charon.*** *Journal of Chromatography A (2020) 1609. https://doi.org/10.1016/j.chroma.2019.460505*

Scientific contact:
agnes.le-masle@ifpen.fr

Two-phase flow simulations: all regimes are now accessible

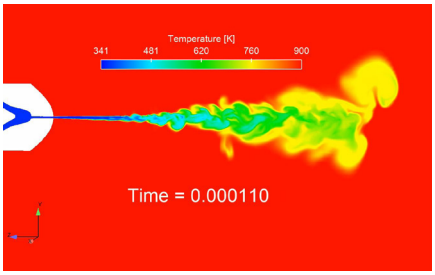
Thesis by Songzhi Yang*

Numerous technological applications requiring the use of numerical simulation involve complex two-phase flows, as is the case with the engine injection context. Most calculation software in the field of fluid mechanics can simulate single-phase (liquid or gas) flows, potentially in a supercritical regime[a], or two-phase flows (liquid-gas) in a subcritical regime.

This research proposes a complete modeling approach to simulate both cases, including the transcritical regime[b], as well as any phase transition (evaporation or condensation). For this, a totally compressible, diffuse interface two-phase flow model was developed, based on a Eulerian-Eulerian approach[c] with real fluids assuming liquid-vapor equilibrium[1]. It made it possible to simulate transcritical injection in the Spray A reference injector of the ECN[d] [2]. It also proved capable of predicting the cavitation phenomenon[e] in a three-dimensional nozzle, thereby highlighting the importance of taking into account dissolved gases in injection modeling[3]. In particular, its use has provided a greater understanding of the phenomenon of bubble nucleation, as a function of the quantity of non-condensable dissolved gases.

Numerous other applications incorporating complex two-phase flows can now be simulated more realistically, such as gas turbines and cryogenic rocket engines, or coolant boiling for electric powertrain power electronics or computing centers.

a - State of a pure body when its pressure P>Pc or its temperature T>Tc. In the opposite case, the fluid is in a subcritical state
b - Condition generated when a subcritical fluid is injected into a supercritical fluid
c - Eulerian approach for both the liquid and gas
d - Engine Combustion Network (https://ecn.sandia.gov/workshop/ECN1/intro.pdf)
e - Formation of gas or vapor bubbles in a liquid subject to a pressure drop



Transcritical injection simulation on the Spray-A injector (temperature field at 112 µs).

*Thesis entitled ***"Modeling of Diesel injection in subcritical and supercritical conditions"***

(1) ***P. Yi, S. Yang, C. Habchi, R. Lugo, 2019.*** *Phys. Fluids 31, 026102. https://doi.org/10.1063/1.5065781*

(2) ***S. Yang, P. Yi, C. Habchi, 2020.*** *Int. J. Multiph. Flow 103145. https://doi.org/10.1016/j.ijmultiphaseflow.2019.103145*

(3) ***S. Yang, C. Habchi, 2020.*** *Phys. Fluids 32, 032102. https://doi.org/10.1063/1.5140981*

Scientific contact:
chawki.habchi@ifpen.fr

Metal nanoparticles living on the edge

Thesis by Ana Teresa Fialho Batista*

Platinum nanoparticles supported on chlorinated γ-alumina are used in bifunctional heterogeneous catalysts[a], which are central to numerous industrial processes. An atomic-scale study, for which different physicochemical parameters were varied, allowed the location of the two types of active sites present in these catalysts and the distance between them to be determined. Both are critical parameters for catalyst performance.

To do so, a multi-technique approach combining synthesis, advanced characterization and modeling (figure) was implemented, with contributions from several IFPEN research divisions and partner laboratories: IPCMS, CRMN, ESRF[b] and Institut Néel.

The HR-HAADF-STEM[c] analyses revealed that sub-nanometric Pt particles and Pt single atoms are present on the alumina[(1)]. Moreover, electronic tomography showed that the majority of Pt nanoparticles are located on the edges of alumina support platelets. This original result is coherent with the NMR and DFT[d] analyses that showed that chlorine is also stabilized on the edges[(2)]. Finally, a mathematical analysis and a geometric catalyst model were used to estimate average inter-site distances.

This improved understanding opens up new catalyst performance improvement routes based on preparation methods targeting active site location tuning on an atomic scale.

a - Comprising active metal sites and acid sites
b - Strasbourg Institute of Materials Physics and Chemistry; High-Field Nuclear Magnetic Resonance Spectroscopy Center in Lyon; European Synchrotron Radiation Facility
c - High Resolution – High Annular Angle Dark Field – Scanning Transmission Electron Microscopy
d - Nuclear Magnetic Resonance and Density Functional Theory

*Thesis entitled ***"Atomic scale insight into platinum based catalysts supported on chlorinated gamma-alumina"***

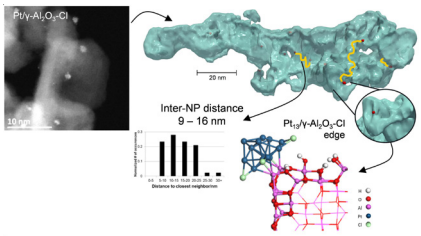


Illustration of study means: STEM image, tomographic volume and molecular model of a Pt nanoparticle on a chlorinated alumina edge.

(1) ***A.T.F. Batista,*** *W. Baaziz,* ***A.-L. Taleb, J. Chaniot, M. Moreaud, C. Legens,*** *A. Aguilar-Tapia, O. Proux, J.-L. Hazemann,* ***F. Diehl, C. Chizallet, A.-S. Gay,*** *O. Ersen,* ***P. Raybaud,*** *ACS Catal. 2020, 10, 7, 4193-4204. https://doi.org/10.1021/acscatal.0c00042*

(2) ***A.T.F. Batista,*** *D. Wisser,* ***T. Pigeon,*** *D. Gajan,* ***F. Diehl, M. Rivallan, L. Catita, A.-S. Gay,*** *A. Lesage,* ***C. Chizallet, P. Raybaud,*** *J. Catal. Priority Communication 2019, 378, 140-143. https://doi.org/10.1016/j.jcat.2019.08.009*

Scientific contact:
ana-teresa.fialho-batista@ifpen.fr

Dynamic flows for better low-carbon strategies

Thesis by Ariane Albers*

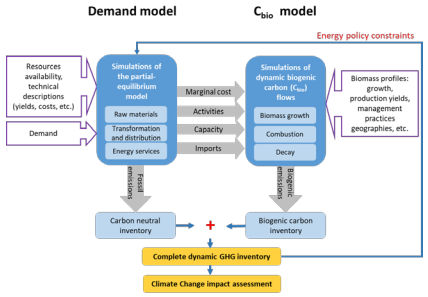
Low-carbon strategies encourage the use of renewable energy sources based, among others, on biomass. The objective of achieving carbon neutrality is expressed *via* a perfect balance between the amount of CO_2 emitted and the amount captured. Emissions impacting climate are analyzed *via* dedicated methodologies, such as life cycle assessment (LCA). However the models used in these approaches are static since they only represent systems in steady-state conditions. But incorporating the time dimension, whereby biogenic carbon (C_{bio})[a] flows are distributed over time, may call into question these low-carbon strategies.

The research conducted for this thesis focused on this very issue, *via* the development of tools to predict dynamic C_{bio} flows and combine them with different demand models (figure). The differences between the results generated by new dynamic evaluations and those derived from traditional static approaches were then analyzed[(1-2)]. The analysis showed that this new C_{bio} sequestration and SOC[b] dynamics modeling approach provided a more accurate representation of C_{bio} flows and that its incorporation into climate change models had a significant impact on forecasts.

This advanced methodology, supporting life cycle analyses, is of particular interest within the context of initiatives to be introduced to tackle climate change.

a - Carbon from the Earth's biosphere
b - Soil organic carbon

*Thesis entitled ***"Incorporation of the time factor in the environmental evaluation of biomass products: Dynamic carbon modeling"***



A prospective energy model combined with a forestry biomass growth model.

(1) ***A. Albers, P. Collet, D. Lorne,*** *A. Benoist, A. Hélias (2019a). Applied Energy 239, 316-330. DOI: 10.1016/j.apenergy.2019.01.186*

(2) ***A. Albers,*** *A. Avadi, A. Benoist,* ***P. Collet,*** *A. Hélias (2019c). Science of The Total Environment, 135278. DOI: 10.1016/j.scitotenv.2019.135278*

Scientific contact:
pierre.collet@ifpen.fr

Reaction dynamics in zeolites under the quantum calculation spotlight

Thesis by Jérôme Rey*, 2020 Yves Chauvin prize-winner

Zeolites are nanoporous solids widely used as acid catalysts for the conversion of hydrocarbon molecules. However, determining the rates of the elementary steps of reaction mechanisms represents a significant challenge, due to the large number of degrees of freedom in the reactants, intermediates[a] and the transition states[b] in the zeolite cavity. This challenge was overcome thanks to quantum calculation techniques.

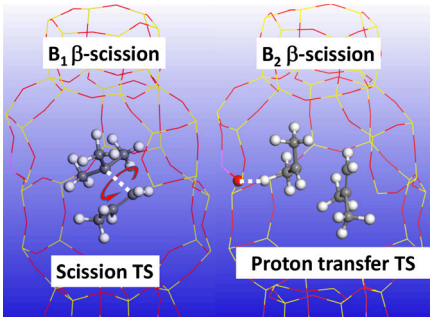
In partnership with Comenius University in Bratislava, we used a constrained[c] AIMD[d] method to precisely model isomerization and alkene cracking reactions, and quantify their rate constants. It turned out that AIMD surpassed traditional static methods for these reactions.

It was thus possible to identify the reaction intermediates involved, as well as the key transition states (figure) for alkene isomerization reactions *via* tertiary[(1)] and secondary[(2)] carbocations[e], and for their cracking *via* β-scission[(3)].

The research resulted in a unique understanding of the mechanisms at work alongside the detailed quantification of the associated rate constants, which directly depend on the free energy different between transition states and intermediates. These will be incorporated in kinetic models to predict the catalytic performances of zeolites on a macroscopic scale, in oil refining and biomass conversion.

a - Products formed and then reconverted during the reaction steps
b - States theoretically present in the reaction process but not concretely observed
c - Making it possible to guide the evolution of the system according to a given reaction process
d - *Ab initio* molecular dynamics
e - Ion derived from an organic compound, with a positive electric charge on one or more carbon atoms

*Thesis entitled ***"Isomerization and alkene cracking mechanisms and kinetics in the chabazite zeolite quantified*** via ***constrained*** ab initio ***molecular dynamics"***



Transition states (TS) determined by AIMD for alkene cracking with 7 carbon atoms in the chabazite zeolite.

(1) ***J. Rey, A. Gomez, P. Raybaud, C. Chizallet,*** *T. Bučko, J. Catal., 373, 361–373, 2019. https://doi.org/10.1016/j.jcat.2019.04.014*

(2) ***J. Rey, P. Raybaud, C. Chizallet,*** *T. Bučko, ACS Catalysis, 9, 9813–9828, 2019. https://doi.org/10.1021/acscatal.9b02856*

(3) ***J. Rey, C. Bignaud, P. Raybaud,*** *T. Bučko,* ***C. Chizallet,*** *Angew. Chem., Int. Ed., 59,18938-18942, 2020. https://doi.org/10.1002/anie.202006065*

Scientific contact:
celine.chizallet@ifpen.fr

News

• ***Gabriele Fioni,*** *the Auvergne-Rhône-Alpes academic region's deputy rector for higher education, research and innovation, visited IFPEN-Lyon to learn about our research in the fields of sustainable mobility and new energies.*

• *Review of advances made by the CARMEN joint research laboratory with* ***an interview-summary by Nathalie Schildknecht,*** *Director Carmen JRL (https://www.ifpenergiesnouvelles.com/article/carmen-jrl-fine-debut-year).*

• ***Antoine Fécant,*** *from the Catalysis, Biocatalysis and Separation Division, spoke at the Lyon Academy of Sciences, Humanities and Arts. His presentation concerned a description of the risks of global warming linked to human activities and particularly uncontrolled CO_2 emissions.*

Scientific event

• ***31st symposium on applied thermodynamics ESAT,*** *4-7 July 2021 - www.esat2021.com*

Awards

• ***Violaine Lamoureux-Var****, from the Geosciences Division,* ***won joint 1st prize in the 2020 FIEEC Carnot applied research awards*** *for Rock-Eval® 7S, a technology used for the geochemical characterization of rock samples.*

• ***Antoine Daudin,*** *from the Catalysis, Biocatalysis and Separation Division,* ***is the joint winner of the 2020 Young Researcher Award*** *given by the French Chemistry Society's Catalysis Division, for his important contribution to the study and development of heterogeneous metal sulfide catalysts and adsorbents.*

• ***The 2020 thesis innovation award*** *given by the Energy Inter-division of the French Chemistry Society's* ***went to Alexis Dubuis,*** *also a candidate for the Yves Chauvin prize (see news item in this issue).*

Publications

• *The IFPEN brochure on fundamental research supporting innovation has just been updated.*

• *Relaunch of the "Cahiers de l'Économie" collection in a digital format. The objective is to present research relating to economics, finance and management for the energy transition, conducted by the Economics and Technology Intelligence Division and by IFP School.*

• *The IFPEN website offers a publication on cobalt, a strategic metal object of its research within the framework of the evolution of energy geopolitics, in the context of the low-carbon energy transition.*

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Contacts:
Scientific Management: Tel. : +33 1 47 52 51 37 - Science@ifpen.fr
Press: A.-L. de Marignan - Tel. : +33 1 47 52 62 07

1 et 4, avenue de Bois-Préau - 92852 Rueil-Malmaison Cedex - France

The detection, at a lower cost, of ultrafine exhaust gas soot particles

Thesis by Adrien Reynaud*

To protect public health, fine particle emissions produced by IC engines have been regulated by the European Union since the 1990s. In order to comply with these standards, particle filters are fitted to the exhaust systems of the vehicles concerned. To ensure they operate effectively, resistive sensors, which are both robust and inexpensive, are excellent candidates. This type of sensor measures the conductance of a particle deposit, forming a kind of bridge between two electrodes (figure). It can currently be used only to estimate a concentration in terms of mass per unit volume. But existing standards also govern the concentration in terms of number, which is a better indicator of the harmful effect of particles on health, taking greater account of ultrafine particles.

As a pre-requisite to the development of a sensor capable of detecting the number, this thesis project set out to gain a better understanding of the mechanisms behind particle deposits, including the finest. Those contained in exhaust gases were first of all categorized in terms of their size using two experimental techniques[a] with a view to only sending the finest among them to the sensor. As a result, it was possible to show that bridge construction also occurred with ultrafine particles (50 nm)[1].

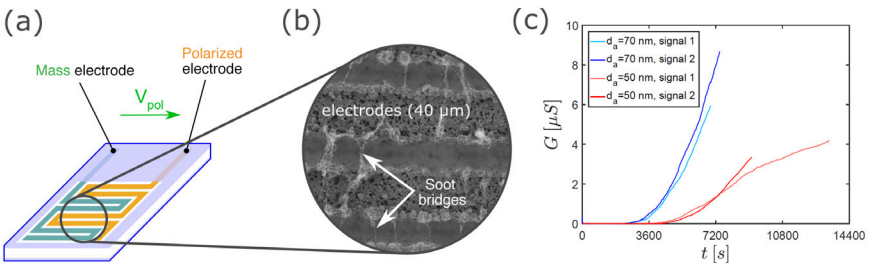


Diagram of the sensor (a), SEM micrograph of bridges (b) and signals for different particle diameters (c).

A numerical simulation analysis then highlighted a physical phenomenon hitherto not covered in the literature in the field, namely dielectrophoresis, which makes it possible to better explain mechanisms governing the construction of soot microstructures as a function of particle size and the principle of which could also be used to develop a sensor capable of detecting the finest particles.

These results represent a significant advance to better exploit the resistive sensor signal, with a view to obtaining information about the concentration in terms of number of ultrafine soot particles.

a - Electrostatic classification and aerodynamic classification

(1) ***A. Reynaud, M. Leblanc, S. Zinola,*** *P. Breuil, J.-P. Viricelle, 2019, Sensors 19. DOI: 10.3390/s19030705*

*Thesis entitled ***"Understanding and modeling of aerosol particle collection mechanisms*** via ***the combination of aerodynamic and electrical phenomena"***

Scientific contact:
stephane.zinola@ifpen.fr

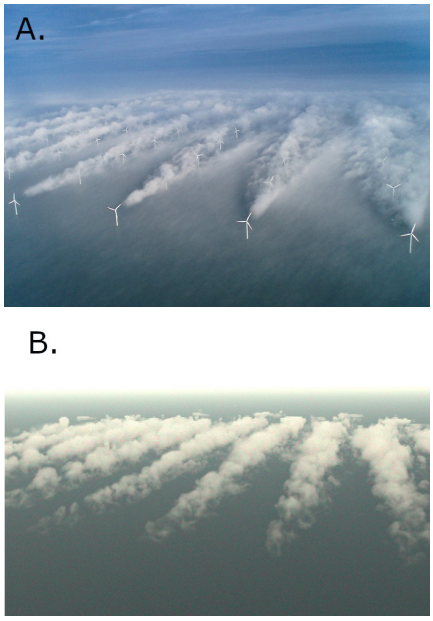
A new numerical tool to simulate the interaction between wind farms and local meteorological conditions

Thesis by Pierre-Antoine Joulin*

The French long-term energy program is encouraging the growth of wind energy. In order to predict this energy production and attempt to optimize it, irrespective of the production site (sea, mountain), a better understanding of wind flow through the farm will be required. This is particularly the case for offshore wind farms that, due to their size, will interact more intensively with the atmosphere and local meteorological conditions. Consequently, characterizing these interactions, which are both multi-disciplinary (aerodynamic and meteorological) and multi-scale (from blade to atmosphere), represents a major industrial and environmental challenge.

A numerical tool dedicated to the problem was developed within the framework of this thesis, in partnership with Météo France. It makes it possible to simulate the behavior of wind turbines within a realistic atmospheric boundary layer. The software is based on the coupling of aerodynamic wind turbine models and Meso-NH, the fine mesh meteorological model developed by the CNRM (French Meteorological Research Center) and the French Aerology Laboratory. The research conducted also set out to validate the results of calculations through comparison with experimental cases)[1]. The capacity to reproduce complex atmospheric conditions was recently demonstrated[2] *via* the cloud formation case at the Danish Horns Rev 1 offshore wind farm, which had hitherto never been reproduced in such detail (figure).

The highly realistic modeling associated with this new, soon-to-be open source numerical tool pushes back the boundaries of what is possible for wind farm simulation. It is already being used by IFPEN to calibrate turbine layout optimization models, as well as to study interactions between wind farms and local weather conditions.



A. Horns Rev farm (Vattenfall; photo: Christian Steiness)
B. Numerical simulation[2]

(1) ***P.-A. Joulin,*** *M.-L. Mayol,* ***F. Blondel,*** *V. Masson, Q. Rodier, C. Lac. (2019, July). Journal of Physics: Conference Series (Vol. 1256, No. 1, p. 012019). IOP Publishing.*
DOI: 10.1088/1742-6596/1256/1/012019

(2) ***P.-A. Joulin,*** *M.-L. Mayol, V. Masson,* ***F. Blondel,*** *Q. Rodier,* ***M. Cathelain,*** *C. Lac. (2020). Frontiers in Earth Science, 7, 350.*
DOI: 10.3389/feart.2019.00350

*Thesis entitled ***"Small-scale modeling of the interactions between wind farms and local weather conditions"***

Scientific contact:
pierre-antoine.joulin@ifpen.fr