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News

Fundamental Research

Yves Chauvin’s work on the mechanisms of olefin metathesis, for which he was awarded the Nobel Prize in Chemistry in 2005, marked a major turning point in our understanding of these mechanisms, providing a springboard for the development of the catalytic processes used in industry today. Through its annual thesis prize, bearing the name of the great man himself, IFP Énergies nouvelles honors not only his memory but also the wealth of knowledge he left to the scientific community. This prize, awarded to a young doctoral researcher who has completed his thesis at IFPEN, is selected by the IFPEN Scientific Board based on criteria of excellence, such as the quality of the work carried out, the progress made in terms of knowledge and methodologies, the impact of research findings, etc. At a time when energy and environmental challenges require bold scientific solutions, the Scientific

Division also intends to use this prize to reaffirm the importance of the research work carried out by PhD students and collaboration with the academic world.
The quality of the many applications submitted each year demonstrates the commitment of IFPEN's research divisions to this award, which clearly reflects our vision of science as a driver of change. The 2025 Prize was awarded to Nicolas FINTZI for his considerable contribution to the “modeling of dispersed-phase two-phase flows,” which will fuel future technological innovations in multiple chemical engineering processes. You can learn more in this issue.

I hope you enjoy it.

Florence Delprat-Jannaud
Scientific Director

LES BRÈVES

Thesis by **Nicolas Fintzi, winner of the 2025 Yves Chauvin prize**: « ***Modélisation statistique des écoulements à phases dispersées : application aux suspensions de gouttes entraînées par la flottabilité*** » **(Statistical modeling of disperse two-phase flows : application to buoyancy-driven droplets suspensions).**

Buoyancy-driven droplet flows are a type of two-phase flow found in many chemical engineering processes, such as gravity separators, liquid-liquid extractors, and flotation columns. It is essential to understand and model these flows in order to optimize the efficiency of the processes in question — for example, by improving phase separation and mass transfer.

The physical systems to be modeled cover a wide range of scales, from the size of droplets (a few micrometers) to that of industrial reactors (often more than a meter). With current computing resources, fully resolving all these scales through numerical simulation would require an excessively long computation time.
Hence, in order to describe the joint evolution of the dispersed phase (the droplets) and the continuous phase (the fluid surrounding the droplets), modern approaches rely on the use of averaged equations. These equations describe the average behavior of the two phases without requiring the complete resolution of the entire flow at local scales.

Furthermore, modeling of dispersed two-phase flows has historically primarily focused on suspensions of spherical solid particles and, to a lesser extent, on emulsions, where the dispersed phase is fluid. Yet, it is this latter situation, where the dispersed phase consists of fluid inclusions, that is found in many industrial and natural contexts (bubble flow, liquid-liquid mixtures, aerosols, etc.).

The main objective of this thesis was to construct a set of averaged equations capable of describing dispersed flows containing fluid inclusions. The dispersed phase was represented by averaged Lagrangian conservation laws, while the continuous phase was modeled by averaged Eulerian conservation laws (see [1]). This system is therefore referred to as a “hybrid model”.

A second aspect of this thesis was the development of closure models to feed into the equations of the “hybrid model” developed[1].

We then used the « Basilisk C » open-source code to perform numerical simulations of emulsions of droplets under gravity (see Figure 1), with the aim of accurately predicting their rheological behavior [2].
Our results, supplemented by theoretical analyses, show that it is essential to include the contribution of the relative velocity between phases, not only in the drag force — the average force exerted by the continuous phase on the droplets — but also in the effective stress[2], including the effects of turbulent fluctuations.

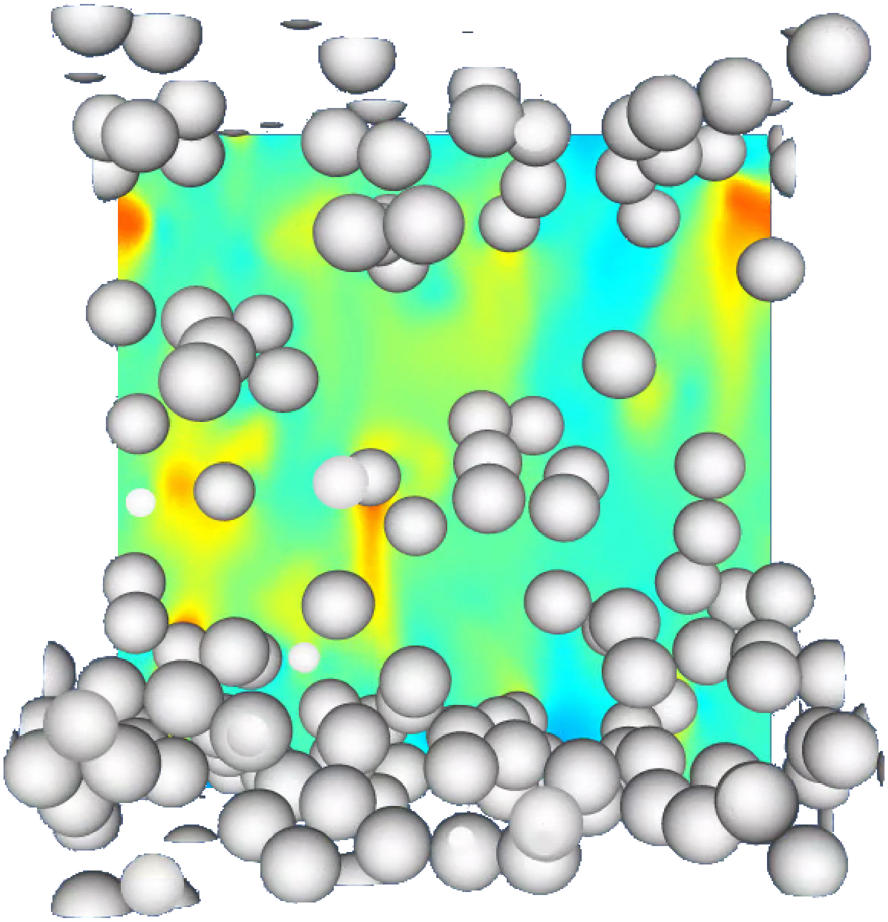

Figure 1 : Typical simulation of a suspension of rising droplets in a tri-periodic box (in color: pressure fields).

Lastly, this thesis also focused on the characterization of the microstructure of emulsions and the study of the relative kinematics of interacting droplets. To do this, we used the nearest neighbor pair distribution function, which describes the probability of finding two droplets at a given distance from one another.
This function was used to analyze the geometry of the microstructure, i.e., the way in which the droplets are organized in space.
We demonstrated that the standard deviation of this distribution is a good indicator for quantifying the formation of clusters, chains, or layers of droplets in the flow [3].

Finally, an equation describing the evolution (in time and space) of the standard deviation of this distribution was developed, enabling analysis of the kinematics of the emulsion microstructure. We showed that the average interaction time between droplets corresponds to the relaxation time[3] of the standard deviation of the distribution of the closest pairs.
This characteristic time is thus a key parameter for describing the microstructure formation.

This work establishes a solid general framework for future research on dispersed two-phase flows, taking into account, for example, coalescence, droplet deformation, or turbulence induced by droplet clusters, all phenomena that are still poorly understood yet essential for process modeling.

[1] These “closure models” allow the flow behavior to be represented at scales not resolved by the averaged equations

[2] Stress observed at macroscopic scale

[3] Time required for a system to return to equilibrium following a disturbance

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References:

1. Fintzi, Nicolas, and Jean-Lou Pierson. ***"Averaged equations for disperse two-phase flow with interfacial transport."*** (Accepted: International Journal of multiphase flows)
   >> arXiv preprint arXiv:2410.10752

2. Fintzi, Nicolas, and Jean-Lou Pierson. ***" Averaged equations for suspensions made of slightly inertial buoyant spherical droplets."*** (submitted).

3. Fintzi, Nicolas, Jean-Lou Pierson, and Stéphane Popinet. ***"Buoyancy driven motion of non-coalescing inertial drops: microstructure modeling with nearest particle statistics."*** Acta Mechanica (2024): 1-24.

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Thesis by **Simon Poirier**: ***« Synthèses en solution d'électrolytes sulfures pour les batteries tout solide »*** **(Wet chemical synthesis of divided sulfides towards All solid state lithium batteries electrolytes)**

Solid-state lithium (Li) batteries offer the promise of surpassing the energy density limits of current generations of Li-ion batteries, while being safer. The key to these performances lies in the choice of the solid electrolyte (SE) and its integration into the electrochemical cell. Among the various SEs studied, inorganic thiophosphate phases (Li?PS? and Li?PS?X with X = Cl, Br, I)[1] are notable for their high ionic conductivity at room temperature (> 10?? S.cm?^{1})1, which makes them suitable for use as solid electrolytes.

Thiophosphates are generally prepared by solid-phase synthesis, combining a milling step and heat treatment. This method produces aggregated micrometric particles. Their integration into hybrid electrolytes (polymer + thiophosphate) or composite cathodes[2] therefore requires an additional mechanical milling step to reduce these aggregates and the particle size. To overcome this, one alternative is liquid-phase synthesis, which is known to offer the ability to control both particle size and morphology. However, it appears that this potential has not been fully exploited in the examples reported in the literature for thiophosphate phases.

An in-depth experimental study of the synthesis of liquid Li_3PS_4/?-Li_3PS_4 phases revealed key parameters for selecting the appropriate synthesis solvent [1] and better understanding the mechanism of Li_3PS_4 phase formation in this solvent (tetrahydrofuran or THF) [2]. This synthesis has limitations, the observation and analysis of which led to the development of two innovative synthesis methods.

The first method, inspired by hot-injection quantum dot synthesis[3], is associated with a 5-fold reduction in the reaction time and, in some cases, eliminates the need for additional heat treatment required to obtain the ionic conductive phase [3]. Morphological control of the particles is achieved through the choice of solvents and/or ultrasound treatment (see Figure 1a and b). This method can be adapted to other phases, such as Li_6PS_5X argyrodites with X= Cl, Br, I [4].

The second synthesis method is based on solvent exchange. Starting from the intermediate Li_3PS_4 ·2THF[4], obtained by synthesis in THF, it enables the formation of a wide panel of new " Li_3PS_4 .xsolvent" intermediates that are not accessible by direct synthesis in the solvents in question. Depending on the choice of solvent, it is possible to control the size, morphology, and ionic conductivity of the final particles (see Figure 1c).

This research has led to advances in the understanding and control of the synthesis of Li_3PS_4/?-Li_3PS_4 phases. A new thesis research project will focus on a more downstream aspect: the impact of particle size and morphology on the electrochemical performance of composite cathodes.

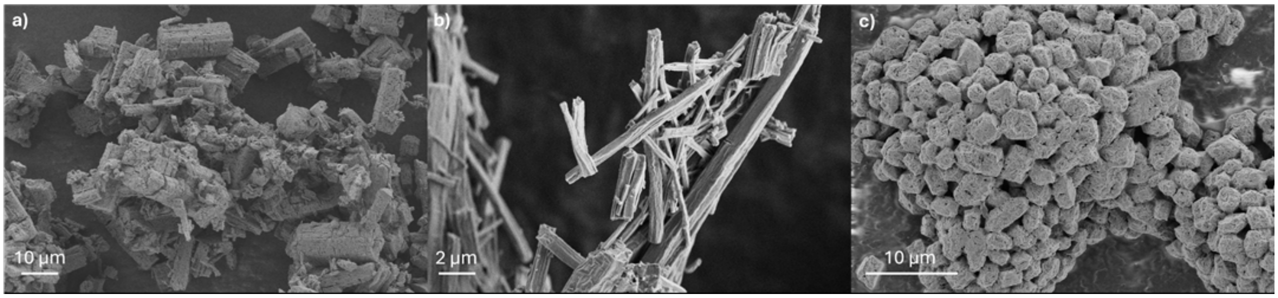

Figure 1: SEM images of Li3PS4 particles obtained by a) conventional synthesis in THF, b) hot injection synthesis, c) solvent exchange synthesis

[1] The Siemens is the unit of measurement for electric conductance in the international system of units. It can be applied to ion conduction

[2] A composite cathode consists of an active cathode material (lithium reservoir), a solid electrolyte, and an electronic conductor (carbon)

[3] Quantum dots are semiconductor nanoparticles whose color depends on their size. The hot injection preparation method allows this property to be controlled

[4] After synthesis of the intermediate Li_3PS_4·2THF, this intermediate undergoes thermal decomposition, leading either to the amorphous Li_3PS_4 phase or to the ?-Li_3PS_4phase

References:

1. R. Poirier, D. Pasquier, A. Lambert, M. Corral Valero, D. Uzio, C. Garnero, ***« Solvent Key Parameters for the Wet Chemical Synthesis of the Li_3PS_4 Solid Electrolyte »***, J. Phys. Chem. C 2024, 128, 28, 11477–11486
>> DOI : https://doi.org/10.1021/acs.jpcc.4c01598

2. R. Poirier, T. Robinson, D. Gajan, A. Lesage, M. Corral Valero, L. Lemaitre, D. Pasquier, A. Lambert, D. Uzio, C. Garnero, ***« Unveiling Insights in the Formation Mechanism of Li_3PS_4 ·2THF Solvato-Complex: H_2S Release and Solvent-Phase Interaction »,*** Inorg. Chem. 2025, 64, 7534?7542
>> DOI : https://doi.org/10.1021/acs.inorgchem.5c00445

3. R. Poirier, C. Garnero, D. Pasquier, A. Lambert, D. Uzio, FR3157375A1

4. R. Poirier, C. Garnero, D. Pasquier, A. Lambert, D. Uzio, FR3157374A1

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Towards better control of thiophosphate electrolytes for solid-state batteries

Thesis by **Claire Bizon Monroc**: « ***Apprentissage par renforcement multi-agent pour le contrôle dynamique de parcs éoliens*** » **(Multi-agent reinforcement learning for the dynamic control of wind farms).**

When wind turbines are assembled on a wind farm, under certain wind conditions they may interact with each other through what is known as the wake effect. When a wind turbine captures the kinetic energy contained in the wind, due to the conservation of energy, the wind flow downstream experiences a decrease in speed and an increase in turbulence. As a result, wind turbines located in this wake see their electricity production fall significantly, while also undergoing increased mechanical fatigue. These wake effects (Figure 1) cause annual production losses of as much as 20%.

It is possible to influence the wakes by controlling specific turbine actuators. Among these, the yaw angle, defined as the angle between the wind direction and the rotor plane, allows the wake to be deflected and thus potentially provides more energy to the wind turbine affected by it (Figure 2). However, to maximize their individual power, wind turbines are positioned perpendicular to the direction of the prevailing wind (i.e., the yaw angle is zero), and decreasing or increasing the value of this angle results in a loss of power for the turbine concerned. The aim is therefore to shift from an individual control strategy to a collective strategy designed to maximize the power supplied on a wind farm scale.

Figure 1: Visible wake effects on the Horns Rev 1 offshore wind farm - copyright Vattenfall.

Finding the combination of yaw angles maximizing production across the entire farm is a challenging optimization problem. Conventional control strategies require modeling of complex aerodynamic interactions between turbines. However, the models are either too rudimentary to produce optimal solutions in the field or too complex to allow for simulations on a farm scale, as the number of turbines increases. An alternative approach consists in using measurements collected in real time on the wind farm: the idea is to design methods capable of learning the optimal combination of yaw angles by observing only the total electricity production.

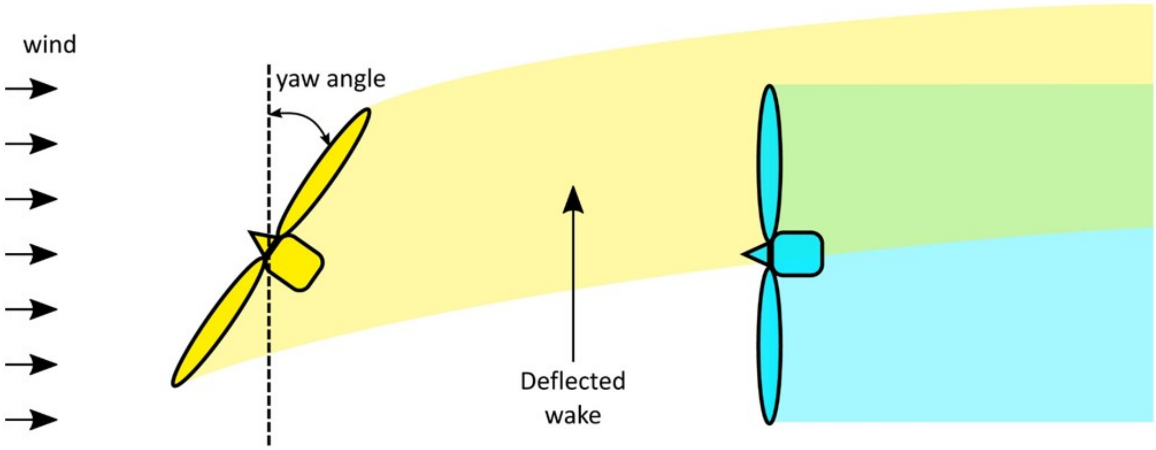

Figure 2: Réorientation de sillage avec contrôle de lacet

However, there are a number of challenges associated with this optimization strategy:

- firstly, wake propagation times, which create a delay between a change in yaw and the point at which its impact on the farm’s production can be observed;
- secondly, the difficulty in measuring the exact contribution of each turbine's yaw change to total production;
- thirdly, these two problems — propagation time and reward attribution — become more complex as the number of wind turbines increases and the size of the research space expands.

In this thesis, wind farm control was framed as a multi-agent reinforcement learning (MARL) problem. Unlike traditional model-based control methods, reinforcement learning (RL) is a method that does not require prior knowledge of physical models. An RL agent learns to make better decisions through trial and error by interacting with its environment. The decentralized MARL approach proposed in this thesis consists in coordinating several RL agents — each agent controlling one turbine — to maximize the farms’ total production.
We proposed several decentralized MARL algorithms [1,2,3]. These algorithms are capable of taking into account the dynamic propagation of wakes in wind farms, and they are easy to apply to a large number of turbines due to their decentralized multi-agent nature. These algorithms were evaluated in reference simulators in the wind energy sector, for farms with between 3 and 36 wind turbines. In all cases tested, they enable a significant increase in production of up to 20% and more compared to the conventional strategy (known as “Greedy”) where all wind turbines are oriented to face the wind (Figure 3).

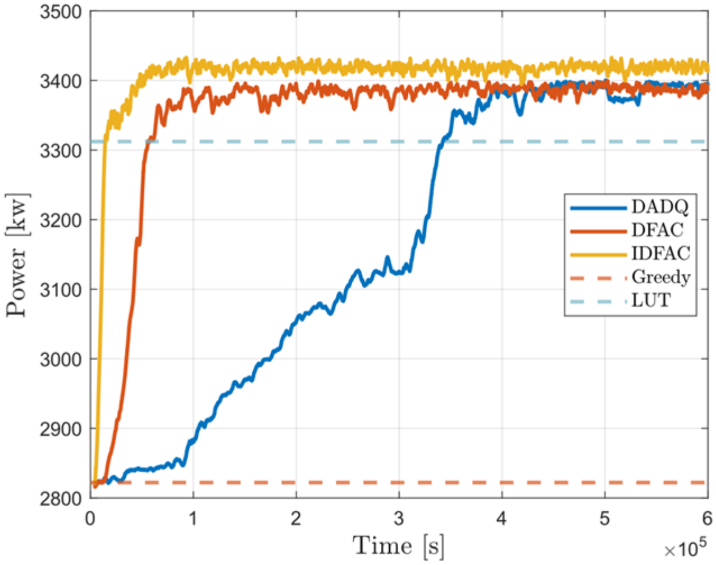

Figure 3. . Evolution of different reinforcement learning algorithms for a wind farm of three turbines. DADQ: Delay-Aware Decentralized Q-learning [1]. DFAC: Delay-Aware Fourier Actor Critics [2]. IDFAC: Imitation-based DFAC [3]. LUT: Look Up Table - obtained by conventional optimization with static models (e.g., Floris)

To facilitate future research into the application of reinforcement learning methods for wind farm control, we have also developed an open-source software library called WFCRL[1] [4]. This enables easy interfacing of control tools widely used by the reinforcement learning community with the FLORIS and FAST.Farm wind farm reference simulators[2].

Finally, from a theoretical point of view, we demonstrated the convergence of a multiscale algorithm within the MARL framework, where agent dynamics can be represented by a DAG (directed acyclic graph) [5]. This result provides a theoretical understanding of the experimental results in the thesis. These results suggest that our RL algorithms could learn online from active wind farms. We are currently continuing our research to further improve convergence time and robustness in windy conditions. We are also working to extend our algorithms to take into account fatigue loads (induced by wakes and turbulence), as well as to enable wind farms to provide services to the electricity grid, for example by following a power signal requested by a grid operator.

[1] https://github.com/ifpen/wfcrl-env et https://github.com/ifpen/wfcrl-benchmark

[2] Both developed by the American National Renewable Energies Laboratory (NREL)

References:

1. Bizon Monroc, C., Bouba, E., Buši?, A., Dubuc, D., and Zhu, J. (2022). ***Delay-aware decentralized q-learning for wind farm control.*** In 2022 IEEE 61st Conference on Decision and Control (CDC). IEEE.
   >> DOI : http://dx.doi.org/10.1109/CDC51059.2022.9992646

2. Bizon Monroc, C., Buši?, A., Dubuc, D., and Zhu, J. (2023). ***Actor critic agents for wind farm control.*** In 2023 American Control Conference (ACC). IEEE.

>> DOI : http://dx.doi.org/10.23919/ACC55779.2023.10156453

3. Bizon Monroc, C., Buši?, A., Dubuc, D., and Zhu, J. (2024). ***Towards fine tuning wake steering policies in the field: an imitation-based approach.*** TORQUE 2024. IOP Publishing.
   >> DOI : http://dx.doi.org/10.1088/1742-6596/2767/3/032017

4. Bizon Monroc, C., Buši?, A., Dubuc, D., and Zhu, J. (2024). WFCRL: ***A Multi-Agent Reinforcement Learning Benchmark for Wind Farm Control,*** NeurIPS 2024 Datasets and Benchmarks Track.
   >> DOI : http://dx.doi.org/10.48550/arXiv.2501.13592

5. (under review at SIMODS, preliminary version presented at ARLET Workshop, ICML 2024) Bizon Monroc, C., Buši?, A., Dubuc, D., and Zhu, J. (2024). ***Multi-agent reinforcement learning for partially observable cooperative systems with acyclic dependence structure.***
   >> https://hal.science/hal-04560319/document

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Multi-agent reinforcement learning for dynamic wind farm control

Thesis by **Sybille Duval-Dachary**: « ***Evaluation du potentiel d'émissions négatives des technologies d'utilisation du CO_2*** » **(Assessment of the negative emissions potential of CO_2 utilization technologies).**

The average global temperature has already risen by more than 1°C. What is to blame? The increase in the concentration of greenhouse gases, including CO_2, in the atmosphere caused by human activities. To limit future increases, technologies known as CCUNET, which combine CO_2 utilization and negative emissions^1 (Figure 1), show great promise: capturing, converting, and then storing CO_2 from the atmosphere would not only reduce atmospheric CO_2 concentrations, but also reduce the extraction of fossil fuels.

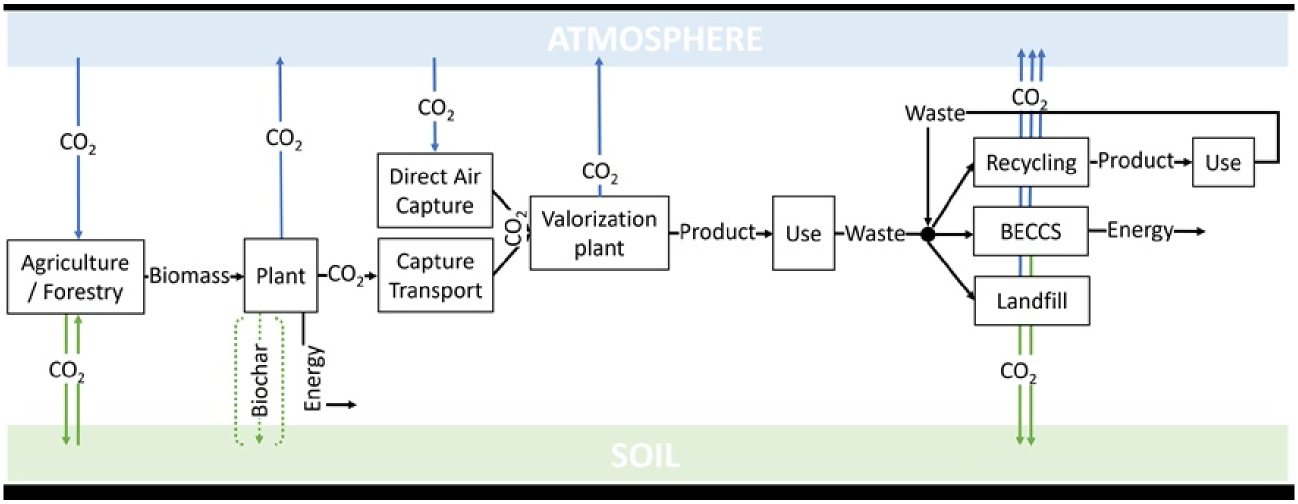

Figure 1: Example of the CCUNET system (BECCS : Bioenergy with carbon capture and storage, Biochar: solid residue obtained by biomass pyrolysis)

However, the environmental benefit of CCUNET technologies is not automatically guaranteed and must be verified using life cycle assessement (LCA). Although mature and applicable to many systems, LCA remains a developing method that seeks to achieve increasingly reliable and meaningful results. In particular, three methodological challenges associated with LCA for CCUNET systems were identified and studied in this thesis:

- Inventory data availability: A review of recent scientific literature on the LCA of bioenergy with CO_2 capture and storage (35 articles) [1] enabled the compilation of generic inventories for biomass combustion and gasification, CO_2 capture based on amine solvents, pipeline transport, and underground storage, thereby expanding the available generic inventories.

- The relevance of existing recommendations for assessing negative emissions: via a case study, the various existing recommendations were compared and their applicability was verified. In particular, this study showed that allocation, a method previously identified as reliable for assessing emissions, can lead to negative scores (CO_2 fixation) being assigned to products within systems where, overall, emissions remain positive. This bias can lead to unfavorable decisions in terms of overall carbon footprint, because an increase in the production volume of a product with “pseudo-negative” emissions will not result in a reduction in the amount of CO_2 in the atmosphere, quite the opposite [2].

- Incorporation of the temporal dimension: in another case study, a dynamic LCA was carried out with the dual purpose of testing and improving the existing tool and assessing the contribution of the temporal dimension to the quality of the results. This exercise showed that, despite the additional effort required to perform a dynamic LCA, it does not necessarily lead to results that are very different from those of a static LCA [3]. A method was thus proposed (illustrated in Figure 2) to enable LCA practitioners to identify, using simplified information, the flows for which the addition of this temporal data is crucial [4].

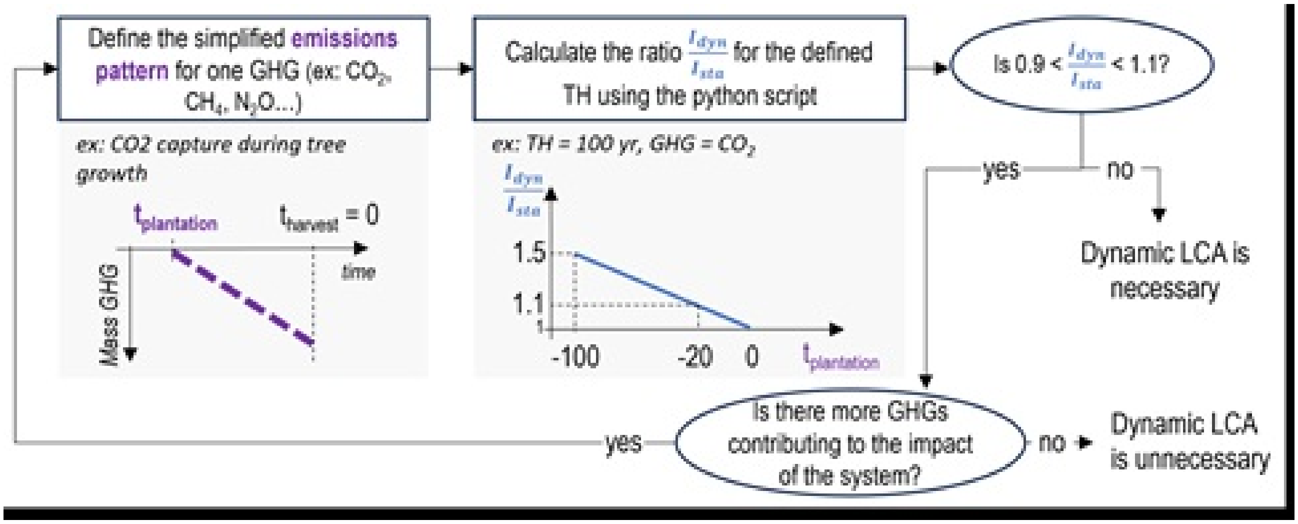

Figure 2: Illustration of the proposed method to enable LCA practitioners to identify, using simplified information, whether a dynamic LCA is necessary.
TH : temporal horizon,
GHG: greenhouse gas,
I_dyn/I_sta : ratio between the impact calculated with a dynamic approach (I_dyn) and the impact calculated with a static approach (I_sta)

In summary, this thesis has made several methodological and practical contributions to improving and facilitating the assessment of CCUNET systems using LCA. Translating the recommendations proposed within the specific framework of carbon accounting would represent a logical next step.

[1] Practices or technologies that enable the permanent removal or storage of CO_2 present in the atmosphere

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References:

1. Duval-Dachary S., Beauchet S., Lorne D., Salou T., Helias A., Pastor A. (2023) ***Life cycle assessment of bioenergy with carbon capture and storage systems: Critical review of life cycle inventories.*** Renewable and Sustainable Energy Reviews 183:113415.
   >> DOI : https://doi.org/10.1016/j.rser.2023.113415

2. Duval-Dachary S., Lorne D., Beauchet S., Salou T., Hélias A. (2025) ***Life cycle assessment of carbon capture and utilisation as a negative emission technology: recommendations and case study.*** International Journal of Life Cycle Assessment 30, 66-78.
   >> DOI : https://doi.org/10.1007/s11367-024-02388-6

3. Duval-Dachary S., Lorne D., Batôt G., Helias A, (2025) ***Facilitating dynamic life cycle assessment for climate change mitigation***. Sustainable Production and Consumption 51, 159-168.
   >> DOI : https://doi.org/10.1016/j.spc.2024.09.017

4. Duval-Dachary S., Beauchet S., Lorne D., Salou T and Helias A., ***Result variations due to dynamic life cycle assessment compared to result variations due to sensitivity analysis on static inventory data*** (2024) SETAC Europe 34th annual meeting (Seville, Spain)

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>> ISSUE 59 OF SCIENCE@IFPEN

Capturing and storing atmospheric CO2: LCA assesses its relevance

Thesis by **Ian Ramtanon**: « ***Exploration de la diversité chimique et des tendances de réactivité enzymatique dans des échantillons complexes de biomasse : approche combinée spectrométrie de masse haute résolution/résonance magnétique nucléaire*** » **(Exploring chemical diversity and enzymatic reactivity trands in complex biomass samples: a combined high resolution mass spectrometry and nuclear magnetic resonance approach).**

Lignocellulosic biomass is a renewable resource for which conversion into bioethanol is a promising avenue for producing alternative, low-carbon fuels. Converting this biomass requires a pretreatment step to break it down. However, this process generates compounds that can inhibit the action of enzymes used to hydrolyze cellulose into glucose, thereby reducing the efficiency of this reaction. In order to improve the profitability of such processes, these inhibitors need to be identified, but their presence in a highly complex environment composed of several hundred products is a real challenge.

The PhD project addressed this issue from the perspective of an innovative multi-technique analytical strategy making it possible to map the chemical diversity of hydrolysates and subsequently propose a methodology for establishing links between the constituents and the observed enzyme inhibition. This strategy is based on a fractionation approach using successive liquid-liquid extraction steps via CPC[1], to simplify the hydrolysates studied, followed by characterization of each fraction by LC-HRMS/MS[2] [1] and NMR[3]. This generates complementary datasets due to the universality of the response of the principal compounds by NMR and the sensitivity of mass spectrometry. The inhibiting properties of the fractions and hydrolysates were then evaluated using enzymatic hydrolysis reactivity tests before the application of chemometric [2] and chemoinformatic methods to analyze these multidimensional data (CPC-LC-HRMS/MS, CPC-NMR, reactivity response).

Considerable chemical diversity was demonstrated, as illustrated in Figure 1 for a hydrolysate. The illustration provided offers a summary overview of the complexity of the sample (each point representing a detected compound) and the main chemical families. The approach also facilitates identification through information propagation, since the identification of a single compound per cluster enables proposals to be made for points in the same cluster (belonging to the same chemical family) and increases the confidence level of groupings through the use of color coding.
Analyses carried out on 22 hydrolysates from a variety of biomass types revealed the combined presence of sugars, organic acids, and phenolic compounds, some of which play a decisive role in enzyme inhibition. Finally, advanced processing of this complex data made it possible to propose candidates with inhibiting propensities concerning enzymatic hydrolysis.

These advances pave the way for new methodological approaches aimed at gaining a better understanding of inhibition mechanisms and optimizing strategies for converting biomass into bioethanol.

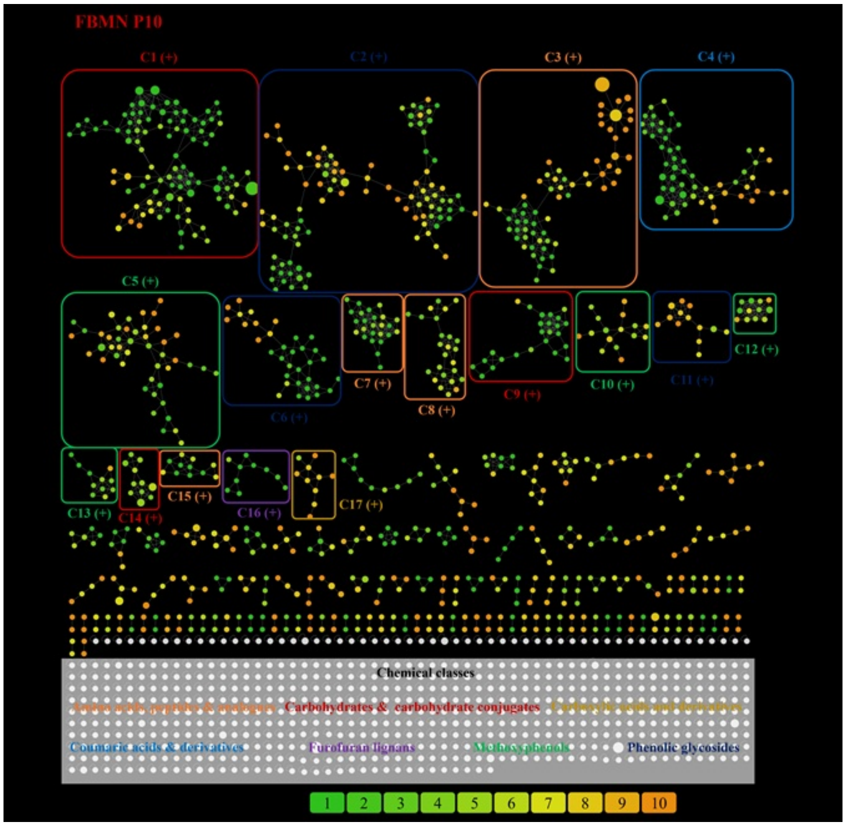

Figure 1: Illustration of LC-HRMS/MS data for a biomass hydrolysate. Each point is a compound, grouped into chemical clusters. Identifying a point in a cluster makes it easier to identify all the compounds in the same cluster.

[1] Liquid-liquid extraction by centrifugal partition chromatography

[2] Liquid chromatography coupled with high-resolution tandem mass spectrometry

[3] Nuclear Magnetic Resonance

References:

1. I. Ramtanon, A. Berlioz-Barbier, S. Remy, JH. Renault, A. Le Masle. ***A combined liquid chromatography – trapped ion mobility – tandem high-resolution mass spectrometry and multivariate analysis approach for the determination of enzymatic reactivity descriptors in biomass hydrolysates***, Journal of Chromatography A, vol. 1706, (2023),
>> DOI : https://doi.org/10.1016/j.chroma.2023.464277

2. I. Ramtanon, M. Lacoue-Nègre, A. Berlioz-Barbier, A. Le Masle, JH. Renault, ***A selective genetic algorithm - PLS-DA approach based on untargeted LC-HRMS: Application to complex biomass samples***, Chemometrics and Intelligent Laboratory Systems, vol. 261, (2025),
>> DOI : https://doi.org/10.1016/j.chemolab.2025.105381

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Link between chemical diversity and enzyme reactivity: multi-technique exploration for bio-based fuels.

Thesis by **Yacine Boudjema**: **« *Effet du catalyseur zéolithique et de la nature du substrat sur les mécanismes de transformations des sucres* » (Effect of the zeolitic catalyst and the nature of the substrate on the mechanisms of sugar transformation).**

Biomass conversion using chemical products and intermediates is increasingly being adopted to reduce the carbon footprint of this industry. Among biomass-based resources, sugars are extremely attractive since they contain a lot of functional groups enabling their conversion into products of interest (alcohols, acids, etc.). This conversion requires the use of catalysts, including heterogeneous catalysts based on zeolites with Lewis acidity[1]**, which have demonstrated strong potential, due to the presence of a tetravalent metal in the lattice position (Figure 1). This is the case with M-Beta zeolites, which can catalyze certain sugar conversions (Figure 2) while offering good recyclability. While at temperatures below 100°C these zeolites are capable of efficiently catalyzing important sugar interconversion reactions**[2]**, at higher temperatures (120-150°C) these zeolites also catalyze retro-aldol reactions, key C-C bond cleavage reactions for the formation of short-chain C2 (such as ethylene glycol) or C3 (such as lactic acid) chemical products. In addition, depending on the sugar undergoing the retro-aldol reaction, C2 products (from glucose), C3 products (from fructose), or a mixture of both (from xylose) are obtained.**

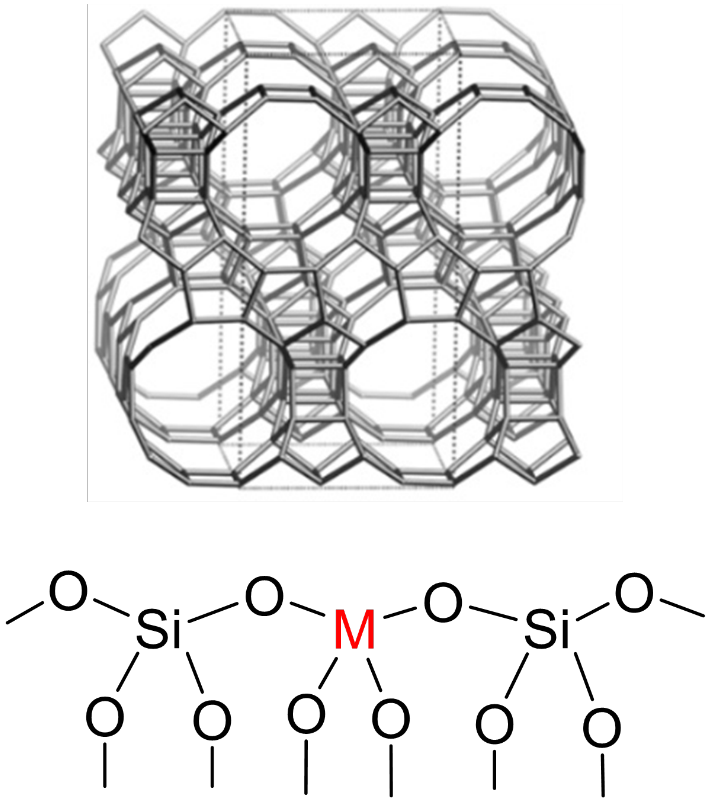

Figure 1: Structure of Beta zeolite, and illustration of metal sites in lattice positions that give it Lewis acidity (M = Sn, Ti, Zr, or Hf).

During this thesis project, which was an integral part of the ANR JCJC[3] SELECTOSZE project, we sought to determine the mechanisms involved in the formation of these various products of interest, as well as the active species involved. To this end, various M-Beta catalytic materials were synthesized (using different preparation methods and different cations). Kinetic measurements of the conversion of the different sugars (glucose, fructose, xylose) were then obtained, supported by sugar isotope labeling strategies (^{13}C)[4] and, in parallel, a molecular modeling study was conducted[5].

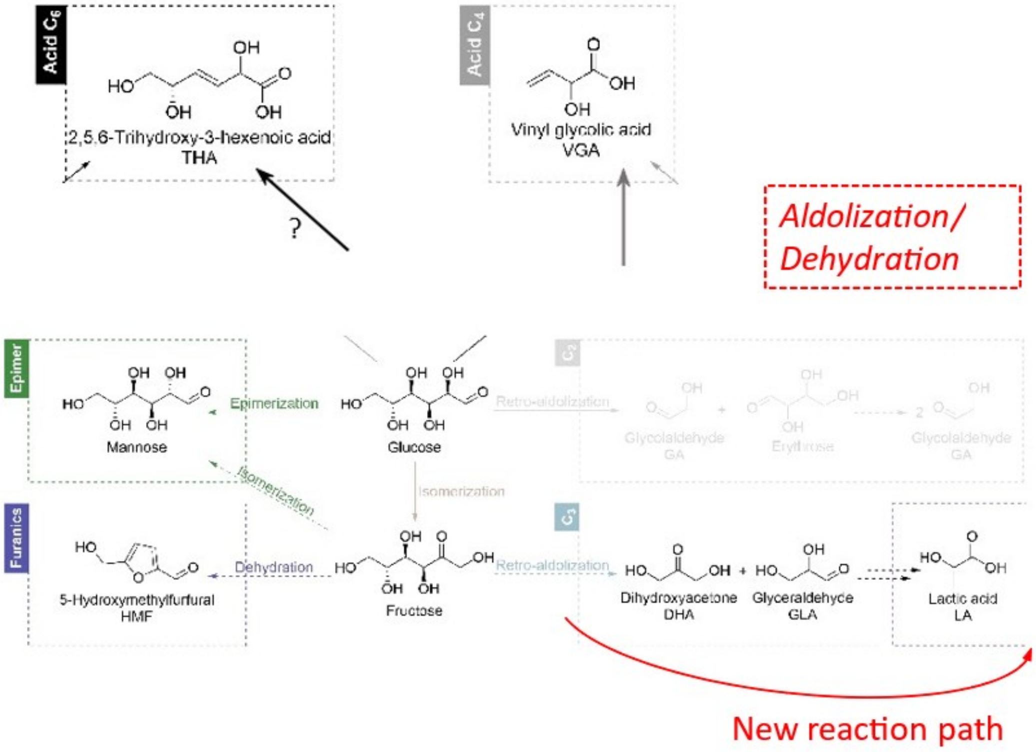

Figure 2: Simplified network of sugar reactions catalyzed by M-Beta

The first component of the research consisted in comparing the catalytic properties and performance of the various synthesized materials. The optimal preparation method, which allows isolated metal sites to be obtained in the zeolite framework and maximum Lewis acidity to be expressed, depends on the metal in question and its precursor[6]. Tin (Sn) is the most active of the metals tested, and is best incorporated into the structure using a solid-state preparation method: by grinding the zeolite precursor (a previously dealuminated Beta zeolite) together with an $SnCl_4$ precursor [1]. It is for this reason that the catalyst was selected as the main candidate for further study.

In parallel, molecular modeling work consisted in establishing appropriate models of the active sites, subsequently enabling mechanistic studies to be carried out. To this end, we generated a large number of models of M sites in lattice positions, for M = Sn, Ti, Zr, and Hf, in three distinct crystallographic sites of the zeolite and for various states of hydration, in order to map their domains of existence as a function of temperature and partial water pressure. This made it possible to identify the most appropriate model as a function of the experimental conditions of the catalytic reaction and to determine the main catalytic characteristics (Lewis acidity, in particular) [2-3].

Lastly, the experimental/theoretical mechanistic study was carried out. Careful examination of reaction products obtained using isotopically labeled substrates led to the discovery of new elements not previously reported in the literature and to the proposal of a new reaction process, the main innovations of which are as follows (Figure 2, in red):

- the production of lactic acid involves a kinetically favored key intermediate called enediol rather than the dihydroxyacetone/glyceraldehyde pair often proposed in the literature.
- the products of the glucose retro-aldol reaction (glycolaldehyde and erythrose) are observed in trace amounts in reaction media, not because this reaction does not occur, but because the products evolve into another compound, vinyl glycolic acid (VGA).

It was also possible to demonstrate the chemoselectivity of the retro-aldol reaction, which favors the conversion of ketoses (fructose, xylulose) over that of aldoses (glucose, xylose). We explained this property at the molecular level based on the specific structures of the various sugars and their modes of adsorption at the active sites [4].

This research has improved our knowledge of both the catalytic materials themselves and the main reactions involved in the conversion of biomass sugars. It has already paved the way for further research in the field of sugar conversion, based on the use of bi-functional zeolite materials exhibiting both Lewis and Brønsted acidity [7].

[1] A Lewis acid is a chemical species that can accept an electron pair and thus create a covalent bond

[2] Reactions involving the isomerization of glucose into fructose, or the epimerization reaction, leading to mannose

[3] A project involving young researchers in France

[4] For monitoring by Nuclear Magnetic Resonance (NMR) spectroscopy

[5] In terms of density-functional theory (DFT)

[6] The precursor is the chemical species containing the metal used to prepare the catalyst

[7] A Brønsted acid is a chemical species capable of donating a proton

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References:

1. Y. Boudjema, A. Brunel, R. del Cerro, G. Pirngruber, C. Chizallet, K. Larmier, ***Relationship between Lewis acid sites and carbohydrate reactivity over Sn-? catalysts***, Catalysis Science and Technology, 2024, 15, 396-404,
   >> DOI : https://doi.org/10.1039/D4CY01147C
2. N. Abidi, Y. Boudjema, C. Chizallet, K. Larmier, ***Investigating Closed and Open Site Stability of Sn-, Ti-, Zr- and Hf-Beta Zeolites: a Comprehensive Periodic-DFT Study***, The Journal of Physical Chemistry C, 2024, 128, 8257-8269,
   >> DOI : https://doi.org/10.1021/acs.jpcc.4c02371

3. N. Abidi, Y. Boudjema, M. Rivallan, C. Chizallet, K. Larmier, ***Challenging the distinction between "open" and "closed" Sn-sites in ? zeolite by deuterated acetonitrile adsorption: experimental and theoretical insights***, The Journal of Physical Chemistry C, 2025, 129, 14011-14019,
   >> DOI : https://doi.org/10.1021/acs.jpcc.5c03670

4. Y. Boudjema, A. Brunel, N. Abidi, G. Pirngruber, C. Chizallet, K. Larmier, ***Mechanistic insights of carbohydrates transformations over Sn-?***, ACS Catalysis, 2025, accepted

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