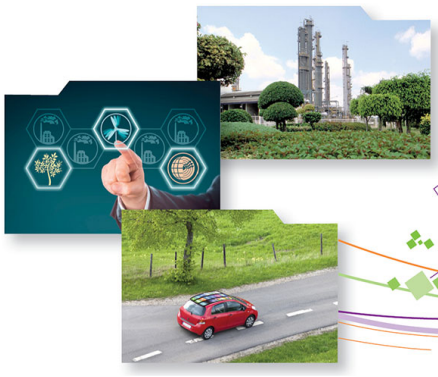

Science@ifpen

Issue 50 - January 2023

Written on 06 January 2023

15 minutes of reading

News

Fundamental Research

For IFPEN, a major research and training player, the annual intake of new PhD students is one of its essential missions.

Doctoral students bring to our fundamental research their dynamism and their capacity to innovate. They also contribute to the necessary development of new skills to meet the scientific challenges inherent to the Research and Innovation projects carried out at IFPEN.

In return, they benefit from a high-quality environment and an openness to concrete challenges and issues that prepare them for their future careers.

Scientific excellence needs to be encouraged and recognized. This is what the **Yves Chauvin prize** does, awarded annually in recognition of the best thesis defended during the year.

By presenting a synopsis of each of the theses short-listed for the award, this special issue highlights the wealth of themes and disciplinary fields covered.

I hope you enjoy reading these articles!

Catherine Rivière
Executive Vice-President IFP Energies nouvelles

LES BRÈVES

Thesis prepared by **Martina Torelli**, winner of the 2022 Yves Chauvin prize*"**Modelling Microbial Methane Processes in Marine Environments: from Source to Seep. Insights from Basin Analysis**"*

Just like carbon dioxide (CO_2), but with a much higher GWP[a], methane (CH_4) is a gas which, according to the IEA[b], is responsible for around 30% of the increase in global temperatures since the industrial revolution.

The biological and abiotic processes that govern its concentration in the atmosphere remain poorly understood. One contribution that is still much debated is that related to the degradation of organic matter contained in marine sediments, at the continental margins[c]. CH_4 escaping from the seabed can mix with sea water and then enter the atmosphere, and some of it can remain stored in the form of gas hydrates. However, depending on local changes in pressure and temperature conditions, these gas hydrates can release massive quantities of methane, contributing to modifications in the chemical composition of the oceans and atmosphere (if they pass through the water column). This result would be a vicious circle: a recent study relating to the southwestern Atlantic [1] has shown that current

ocean warming may amplify this phenomenon by causing the long-term destabilization of these gas hydrates.

To date, the quantities of CH_4 actually reaching the atmosphere from the seabed are uncertain and probably underestimated. Estimates vary between 3% and 9% of global emissions [2], based on insufficient available data obtained from petroleum exploration and scientific drilling campaigns.

Large-scale modeling is proving to be a useful additional tool for understanding and quantifying past and present flows from the seabed likely to merge with sea water and potentially enter the atmosphere, thereby gradually altering their composition.

With its expertise in the field of sedimentary basin modeling and simulation, IFPEN hosted a PhD thesis on the subject, within the framework of the PAMELA (PAssive Margins Exploration LAboratories) research program [3][d]. An original approach, using the TemisFlow™ software, was used to evaluate the quantities of gas generated in the seabed, following the microbial decomposition of organic matter, as well as the quantity trapped in the form of carbonates, in order to determine the evolution in time of carbon flows (CH_4 et CO_2) in natural seabed conditions.

This research was an opportunity to explain the processes of alteration of sedimentary organic matter [4] and the strategy adopted then consisted in constructing a model coherent with the basin geology:

- incorporating the geological history as well as data characterizing the sedimentary organic matter (SOM);
- describing the processes involved in the formation/migration and trapping of microbial gases.

This approach has been applied to the Aquitaine basin (Bay of Biscay) [5] and is illustrated in the figure below. The modeling results show that current methane flows (27 Mg CH_4/year) are similar to those estimated from in-situ flow measurements and acoustic data (35 Mg CH_4/year) [6].

By demonstrating the ability of a simulation tool initially developed for petroleum exploration purposes to describe large-scale complex phenomena likely to amplify climate change, this research illustrates IFPEN's policy of using its resources to meet new challenges.

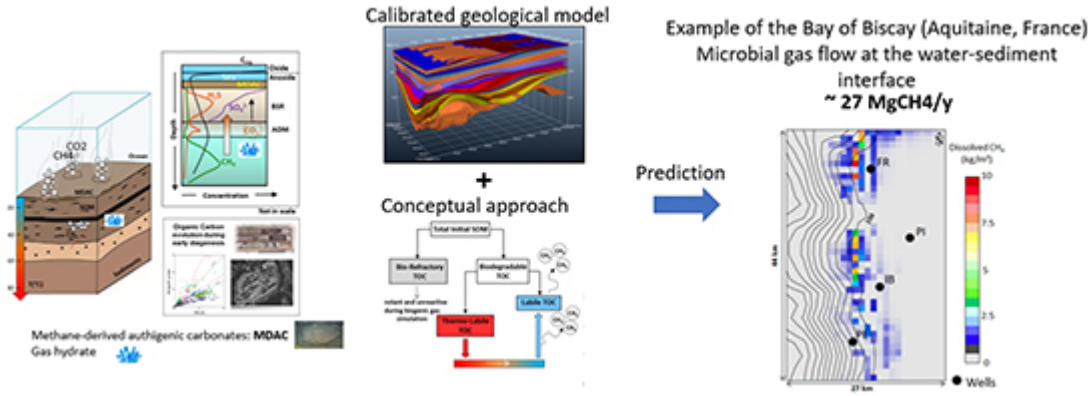

Figure: Use of a tool developed at IFPEN for oil exploration (TemisFlow TM) for climate-related studies: large-scale estimation of carbon flows at the water-sediment interface

a- global warming potential: the heat absorbed by any greenhouse gas in the atmosphere as a multiple of the heat absorbed by the same mass of carbon dioxide.
b- IEA (2022), Global Methane Tracker 2022, IEA, Paris >> https://www.iea.org/reports/global-methane-tracker-2022, License: CC BY 4.0
c- underwater zone located at the edge of continents to where the vast majority of the sediment generated by continental erosion is transported.
d- also involving TOTAL Energies, IFREMER, the CNRS and the Universities of Western Brittany (UBO), Rennes 1 and Paris VI.

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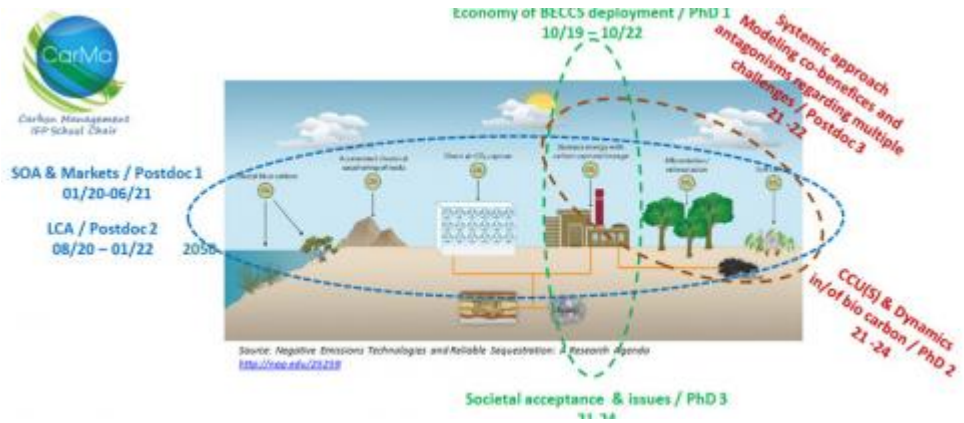

CarMa Chair: negative CO2 emissions by 2050

Tackling climate change necessarily involves reducing greenhouse gas emissions resulting from human activities, primarily carbon dioxide and methane. The problem is global and the actions required must be implemented within the framework of a systemic approach, with scale effects that are difficult to fully understand. Nevertheless, the Paris Agreement reflects the determination of nations to correct the current trajectory while respecting the legitimate aspirations of emerging countries to raise their living standards.

Economics | **Forecasting and scenario modeling** | **Environmental impact evaluation & LCA**

Natural gas in marine sediments: a climate issue?

Thesis prepared by **Julien Petit**:*"Exploration of a new ethylene oligomerization reactivity – Towards dicationic nickel complexes"*

The olefin oligomerization reaction provides access to a broad range of key compounds in the fuel, petrochemical and fine chemistry sectors.

In these different contexts, the rich and unique reactivity of nickel with unsaturated compounds has made this metal one of the principal success stories for this family of catalytic processes. On an industrial scale, the selective oligomerization of ethylene to 1-butene, 1-hexene or 1-octene (intermediates in the manufacture of different grades of polyethylene) respectively currently uses metals such as Ti and Cr. In this field, Ni-based catalysts are not yet used since they are too rarely selective to a single olefin and sometimes highly isomerizing, which reduces the quality of the ?-olefins produced (required purity > 99.3%).

PhD research conducted at LHFA[a] (University of Toulouse) and IFPEN was aimed at studying the possibility of having these nickel catalysts function according to a mechanism known as “oxidative coupling”, recognized as being more selective but yet to be demonstrated for this metal [1]. On the basis of preliminary theoretical calculations (using DFT[b]), it was possible to identify the [L_nNi^{2+}] fragment (dicationic Ni(II) complex associated with n L-type ligands) as a potential intermediate for the oxidative coupling of two ethylene molecules, in order to obtain 1-butene selectively.

While dicationic nickel (II) species are reported in the literature, they are generally stabilized by at least four L-type strong electron donating ligands, preventing any ethylene molecule from coordinating at the metal center (Ni^{2+}). This research thus set out to design access paths to [L_nNi^{2+}] species, with at least two coordination sites accessible for ethylene. Access to these Lewis acid compounds[c] was explored using diverse approaches (Figure).

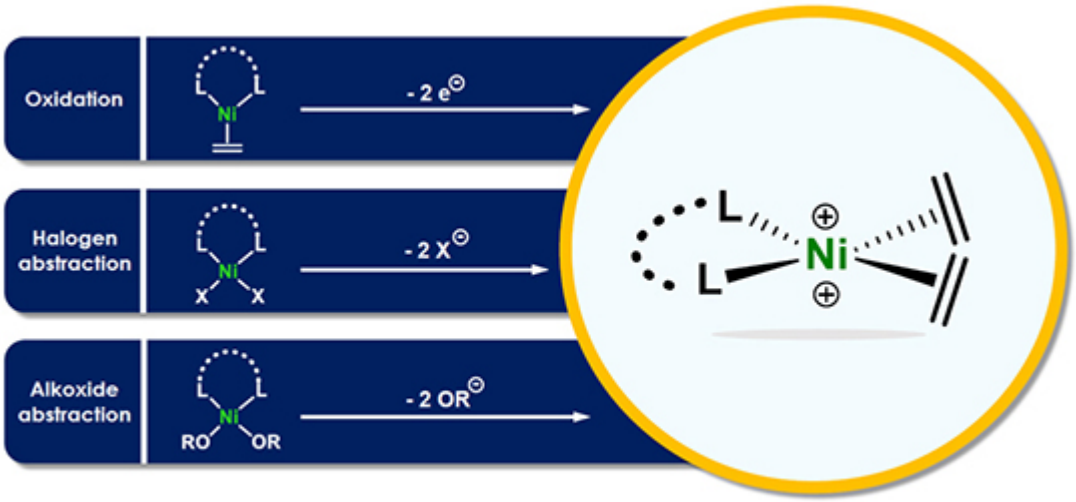

Figure: [L_nNi^{2+}] complex access strategies

[L_nNi^{2+}] complexes, little described in the literature, were synthetized and totally characterized by a combination of techniques: NMR, mass spectrometry, X-ray diffraction as well as DFT studies. They were then employed in ethylene oligomerization reactions. Remarkably, some complexes were found to be active for butene production, paving the way for a new reaction path that could not yet be totally identified at this stage, however [2]. This highly exploratory research confronted nickel with what remains an extremely challenging fundamental objective today.

In 2021, Julien Petit was awarded the French Chemical Society's Coordination Chemistry Division prize.

a- LHFA: *Laboratoire Hétérochimie Fondamentale et Appliquée* or Fundamental and Applied Heterochemistry Laboratory.
b- DFT: Density-functional theory.
c- Species likely to accept an electron pair.

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Chemical sciences

The quest to find a new reaction path for the oligomerization of ethylene using nickel

Thesis prepared by **Philippe Gantzer**: *"Development and comparison of inverse QSPR-inverse approaches "*

What chemical engineer has never dreamed of having access to a tool that can directly identify a fluid (pure substance or mixture) on the basis of characteristics necessary to a given application context? This Holy Grail could become a reality thanks to the field of Chemoinformatics and its methods.

Cheminformatics lies at the interface of several scientific fields and involves using computer and information science techniques to solve problems related to chemistry. One application involves using artificial intelligence to predict usage properties on the basis of reference data, relative to composition or structure [1]. Using machine learning, it is thus possible to establish models that are bridges between molecular descriptors and properties of interest. In addition to this predictive use, chemoinformatics can be used in screening processes[a], or even be part of an inverse approach, i.e., to propose molecular structures likely to satisfy certain constraints.

With this in mind, the specific aim of this PhD research was to develop a molecular structure generation method. Having identified the different methods in the literature [2], two approaches were selected: **the concatenation of molecular fragments (CFM) and the evolution of molecular structures (ESM)**. The first consists in identifying molecular fragments and then combining them, while the second consists in changing molecular structures via the application of different operators, such as atom hybrids or mutations, bonds or functional groups. Once implemented in numerical form, these approaches were compared with one another using a specific approach.

There are, in fact, numerous criteria for evaluating the predictive quality of a model describing properties, but very few existed for new structure generation methods. To overcome this, we proposed a specific approach as illustrated in the figure below. This consists in projecting virtual molecular structures in the “chemical space” – a multidimensional space based on molecular descriptors -[b] (and reduced to three dimensions here) – and then comparing these projections on the basis of indices reflecting their degree of occupation[c] or coverage[d] of this space [3].

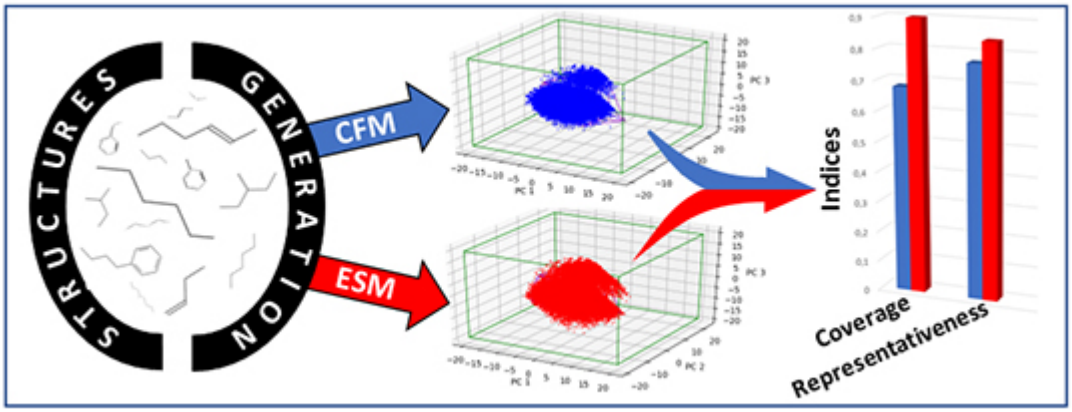

Figure: Comparison of molecular structure generation methods, figure adapted from reference [3].

The comparisons made on the basis of these new indices showed that the ESM approach is more effective than the CFM method. If offers better coverage of the chemical space and is thus capable of proposing a greater diversity of new structures meeting given specifications.

Therefore, it is this method that is going to be used in different application contexts, such as to identify new solvents.

a- Identification of molecules in an existing base.
b- Such as a breakdown of functional groups.
c- Quantity of elementary cubes occupied.
d- Individual population of elementary cubes.

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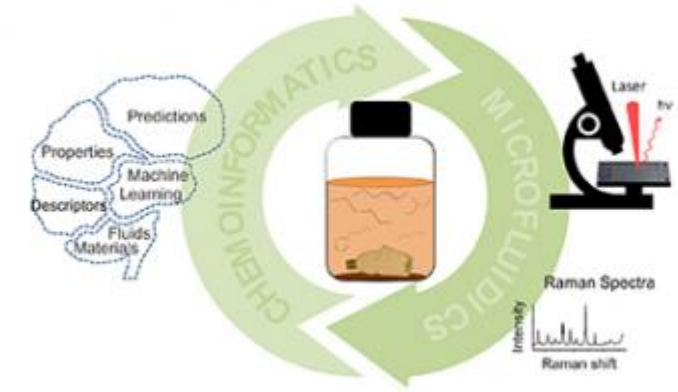
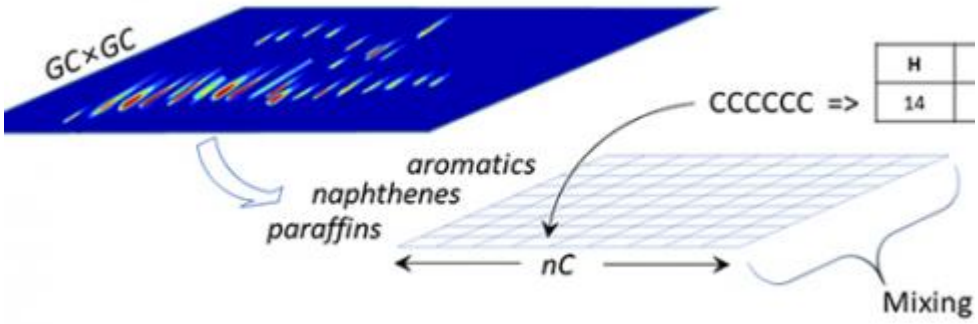


Microfluidics and Chemoinformatics: a highly complementary approach to studying material/fluid compatibility

Pour de nombreuses applications industrielles, comme le recyclage chimique des plastiques, ou encore pour assurer la compatibilité entre polymères et nouveaux carburants, il est essentiel d’anticiper les interactions entre matériaux et fluides...

Chemical analysis | **Microfluidics** | **High-throughput experimentation (HTE)** | **Signal processing/Data science**



Cheminformatics and its descriptors: application to polymer/fluid compatibility

Ensuring compatibility between polymers and fluids is essential in numerous industrial sectors: in the automotive sector, for example, the resistance of materials used in the fuel supply system is a vital consideration.

Chemical analysis	Thermodynamics/Molecular modeling	Signal processing/Data science

The in silico creation of molecular structures

Thesis prepared by **Edoardo Basilico**: *"Carbon steel corrosion scales protectiveness study in CO_2 aqueous solution"*

Due to their low cost and their good mechanical properties, carbon steels are a widely used material, including for equipments in contact with harsh environments, such as aqueous media containing CO_2. In the latter, carbon steels are subject to uniform corrosion, resulting in some conditions to the formation of a pseudo-passive layer[a] of iron carbonate on its surface, which protects it and stops the process.

However, sporadic contamination of the environment by oxygen can alter this protection and affect the reliability of installations exposed to this risk. The effect of some environmental parameters (composition of the water and the gaseous atmosphere) on the pseudo-passivation phenomenon thus represents a major challenge for the technological processes concerned[b].

The influence of the composition of the corrosive environment was the focus of this thesis. The research was conducted within the framework of an experimental program in which parameters were varied around a reference condition leading to pseudo-passivation [1]. A combination of several experimental techniques was deployed[c] making it possible to show that the pseudo-passive layer was composed almost uniquely of siderite ($FeCO_3$), with the possible presence of a magnetite precipitates (Fe_3O_4) at the inner interface between the corrosion scale and the steel.

The impact on the pseudo-passive layer of contamination of the environment by oxygen traces was evaluated by varying its concentration between 90 and 300 ppb[d] . The presence of oxygen modifies the mode of corrosion, shifting from a global and uniform attack to a localized corrosion, characterized by pits. Within these pits, phases other than siderite form, such as chukanovite ($Fe_2(OH)_2CO_3$).

These results were then modeled using a mechanism [1, 3]: a first step is the formation by oxygen of cavities in the siderite layer formed prior to contamination (Figure 1). In these cavities, the oxygen is consumed and an oxygen depletion is produced, creating differential aeration conditions between the cavity and the rest of the deposit and the chukanovite formation.

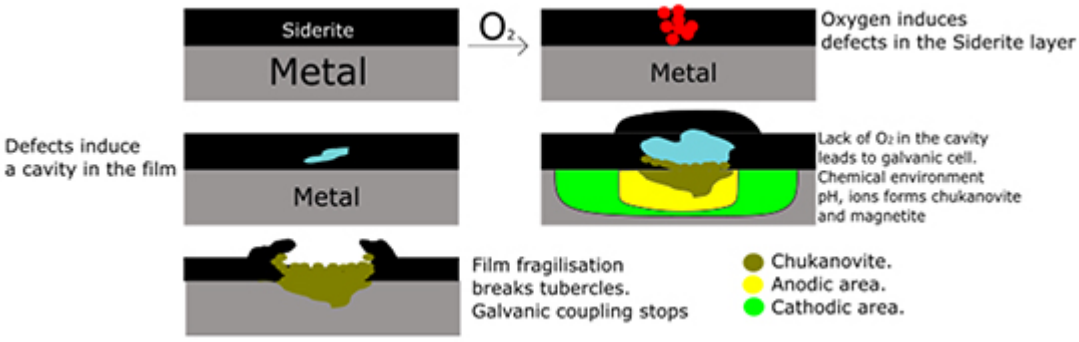


Figure 1: Illustration of the localized corrosion mechanism via pitting in the presence of oxygen.

In addition to the mechanism involved, the results of this study highlighted the existence of an threshold oxygen concentration, below 90 ppb of oxygen, to initiate localized corrosion of the pseudo-passive surface. However, an important practical point is that when contamination stops, a pseudo-passive layer is reformed, restoring excellent corrosion resistance (Figure 2).

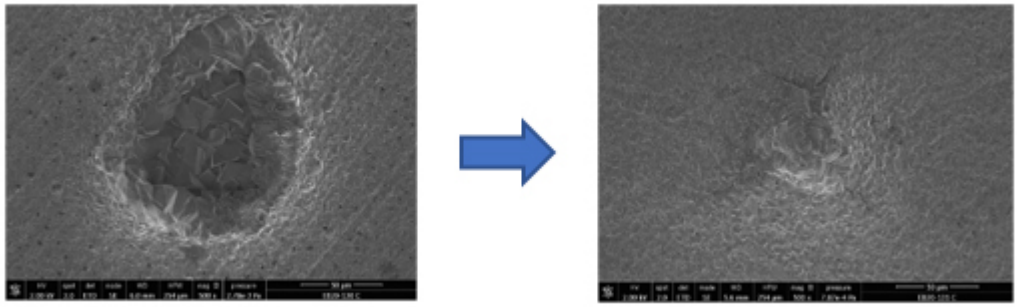


Figure 2: SEM images of the reformation of a pseudo-passive layer on a pit following discontinuation of oxygen contamination.

a- A layer with a thickness of a few microns, made up of corrosion products, which acts as a shield against the transport of iron ions into the solution.
b- For example: CO_2 capture, transport and conversion, underground gas storage, conversion of biomass into fuels and chemicals.
c- Electrochemical impedance measurement, surface chemical analysis and local pH measurements.
d- i.e., contamination of 0.5 to 1.8% of oxygen in the gas.

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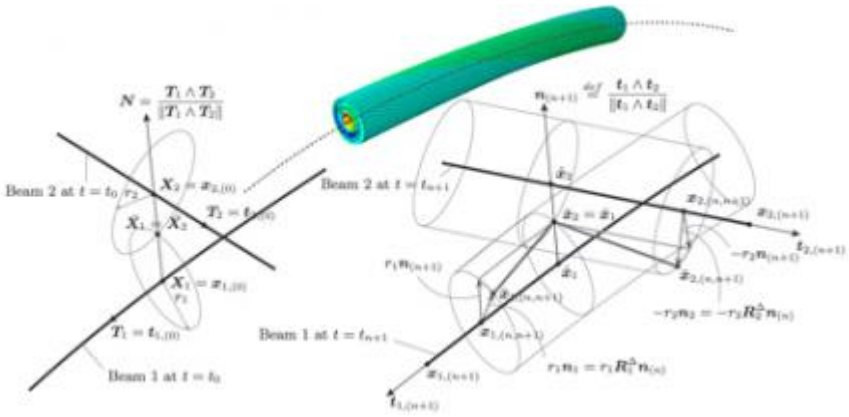

“From material to structure” modeling: the case of anchor cables for offshore wind, in corrosive environment

Anchor lines, the majority of which are carbon steel cables, are essential components for the stability of offshore floating structures, such as those supporting wind turbines. To overcome the risk of breakage during service, redundant lines are generally incorporated at the design stage, which adds significantly to the cost...

Mechanical and thermal testing | **Solid mechanics** | **Numerical methods and optimization**

Innovation and Industry

News September 2021

The French Corrosion Institute and IFPEN sign a framework partnership agreement relating to the energy transition

Press release

Renewable energies | Responsible oil and gas

Physical chemistry | Electrochemistry and corrosion

Self-repair against localized corrosion

Thesis prepared by **Maxime Carrié**: ***"Study and modeling of biofilm IBE fermentation"***

The market for biobased alcohol is currently largely focused on the production of ethanol for use in biofuels. C3 and C4 alcohols are platform molecules for biobased chemistry, but their development is hampered by low productivity levels due to the limited tolerance of microorganisms to these metabolites.

One strategy to increase these productivity levels consisted in developing a continuous production method combined with a biomass retention system within the reactor. Its principle, patented by IFPEN [1], hinged around exploiting the natural capacity of the microorganism to grow in the form of a productive microfilm. The latter immobilizes the bacterial cells, thereby increasing the residence time and concentration of bacteria in the reactor, resulting in a volume productivity multiplied by 4. However, this atypical and innovative approach creates many challenges in terms of understanding its scale-up, particularly since productive biofilms have received little coverage in the literature.

The thesis research related to the characterization of this type of biofilm via new approaches using flow cytometry[a] [2] and confocal microscopy[b] (Figure). Using these methodologies, the evolution of the viability of the biofilm formed over time was described. In parallel, a temporal metabolite production model was developed. This makes it possible to describe continuous immobilized fermentation via a set of 15 equations. Moreover, by creating and exploiting an experimental database of immobilized fermentation, it was possible to identify the key parameters for the model, which was then implemented in a numerical tool.

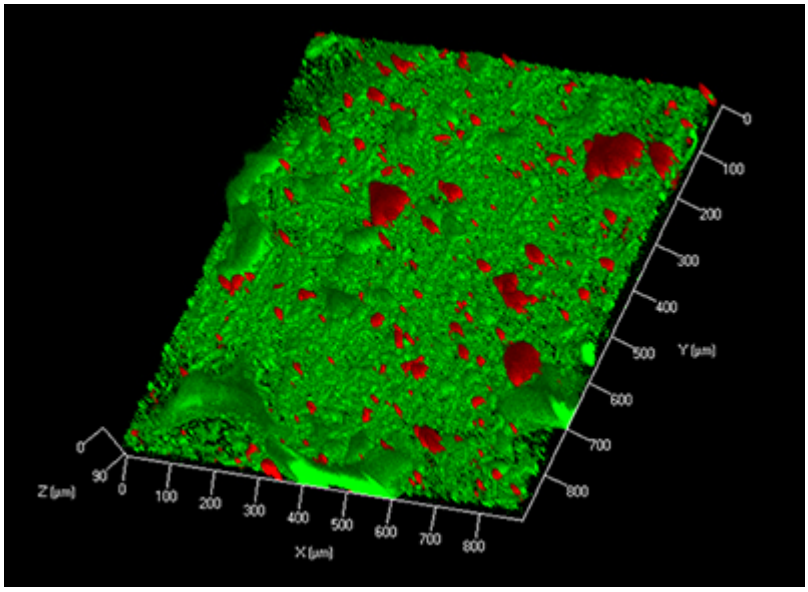

Figure: Image of a clostridium beijerinckii biofilm produced by confocal laser scanning microscopy (x100)

This numerical tool [3] accurately describes the phenomena at play (biofilm growth, molecule production[c]). It describes cell detachment and attachment phenomena, in the bioreactors, as well as the ramp-up and associated volume productivity.

This research has led to a significant improvement in knowledge of biofilm formation and paves the way for a better understanding of the immobilized process. In turn, this will lead to improved process control and , both in terms of reproducibility and optimization of volume productivity.

a- individual, quantitative and qualitative characterization technique for particles suspended in a liquid.
b- making it possible to produce images with a very shallow field depth.
c- isopropanol-butanol-ethanol.

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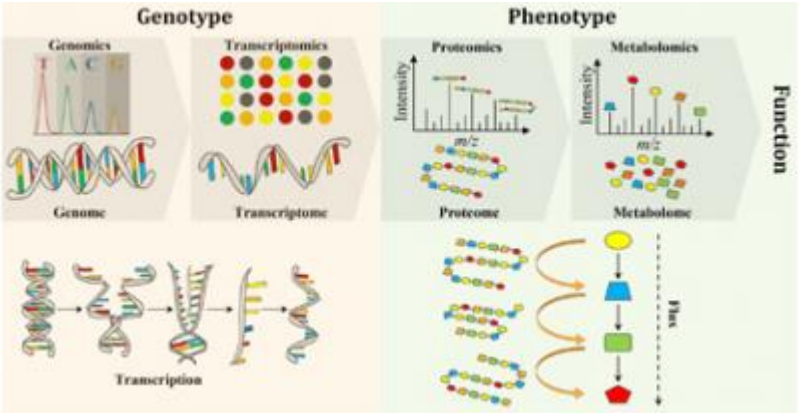

The “Omics”, seven hired hands working for biotechnology

Most frequently, the use of a microorganism in the production of biofuels or biosourced chemicals requires its optimisation. This is achieved through genetic engineering, which involves inactivation and/or addition of one or more genes, to improve the ability of this microorganism to produce a target molecule. (...) At IFPEN, access to genomics (DNA) has helped in gathering data on the composition and structure of the genomes of the microorganisms...

Biosciences and biotechnologies | **Microbiology** | **Genomics** | **Biocatalysis**

Biofilm development of bacteria for the production of biobased C3/C4 alcohols

Thesis prepared by **Delphine Herrera**: *"Characterization and kinetic studies of the formation of bicontinuous microemulsions - Impact of asphaltenes"*

In the context of the energy transition, it is expected that oil production will decrease at the same pace as the development of low-carbon energies and people's evolving needs in this area.

During this transition, it appears to be far more pertinent to seek to extract more oil from existing fields rather than to bring new fields into production.

Hence the importance attached to enhanced oil recovery or EOR. This practice consists, for example, in injecting aqueous surfactant solutions that will enable the formation of microemulsions, thereby eliminating the capillary forces opposing flows in the porous media of the reservoir. These thermodynamically stable microemulsions take the form of bicontinuous mixtures (Figure 1).

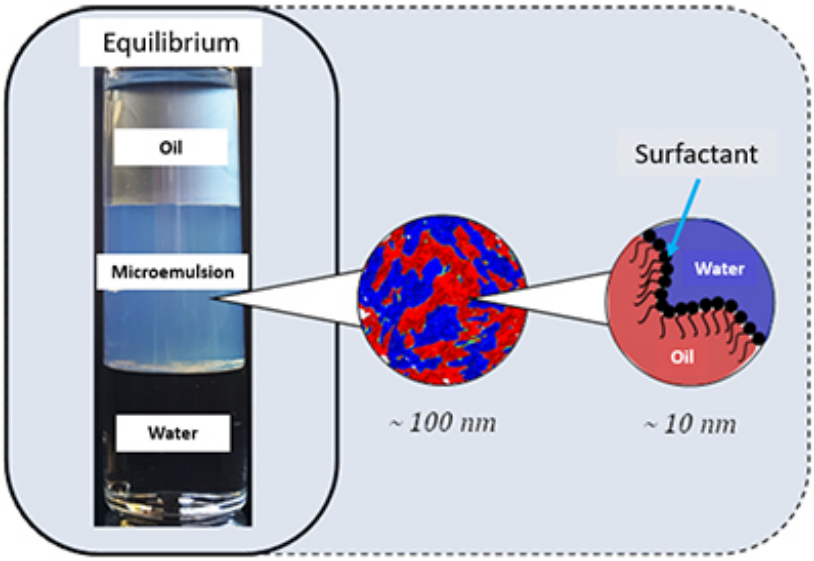

Figure 1: Example of bicontinuous microemulsion; the image in the center illustrates the bicontinuous phase or sponge phase on a scale of 100 nm; the image on the right illustrates the interfacial film, made up of surfactants, separating the oil and water in this bicontinuous phase on a scale of 10 nm.

The formulation of solutions to be injected is chosen in such a way as to maximize the mobilization of hydrocarbons trapped in the reservoir rock. The choice is made in the laboratory on the basis of criteria relating to the stability of the microemulsions formed and interfacial stresses. However, when conducting tests with real crude oils, the visualization of the microemulson tends to be challenging due to its opacity and its poorly defined interfaces with the excess aqueous and oil phases. Researchers are thus faced with a number of difficulties when trying to characterize the target properties and ensure they have before them a genuine thermodynamically stable microemulsion system. Moreover, few approaches provide access to the formation kinetics relating to these complex systems, especially in reservoir conditions.

It is therefore necessary to conduct these tests on microemulsions that are based on model oils, supposedly equivalent to the crude to be extracted[a]. However, the question of how representative the microemulsions formed are compared to actual cases arises, in the absence of surfactants, particularly asphaltenes, which are naturally present in hydrocarbons. Moreover, this difference in composition means it is not possible to guarantee the microemulsion formation kinetics are similar to those that would actually be produced following injection into the reservoir.

In order to make progress in the characterization of complex microemulsions and the understanding of factors influencing their formation, a PhD thesis was undertaken adopting a multi-scale approach, from interface structures (on a nanometric scale) through to the global behavior of the microemulsion.

The research initially focused on the development and implementation of non-destructive characterization methods - NMR, Microscanner, SAXS and DLS[b] - aimed at gaining a better understanding of the mechanisms involved in the formation of model and asphaltene microemulsions.

In terms of methodology, a new NMR application was specifically developed for this study and good agreement was found with another original X-ray tomography approach [1]. NMR is one of the few methods adapted to opaque or dark systems for the determination of the compositions of the different phases simultaneously, rapidly and locally. A result example is shown in Figure 2.

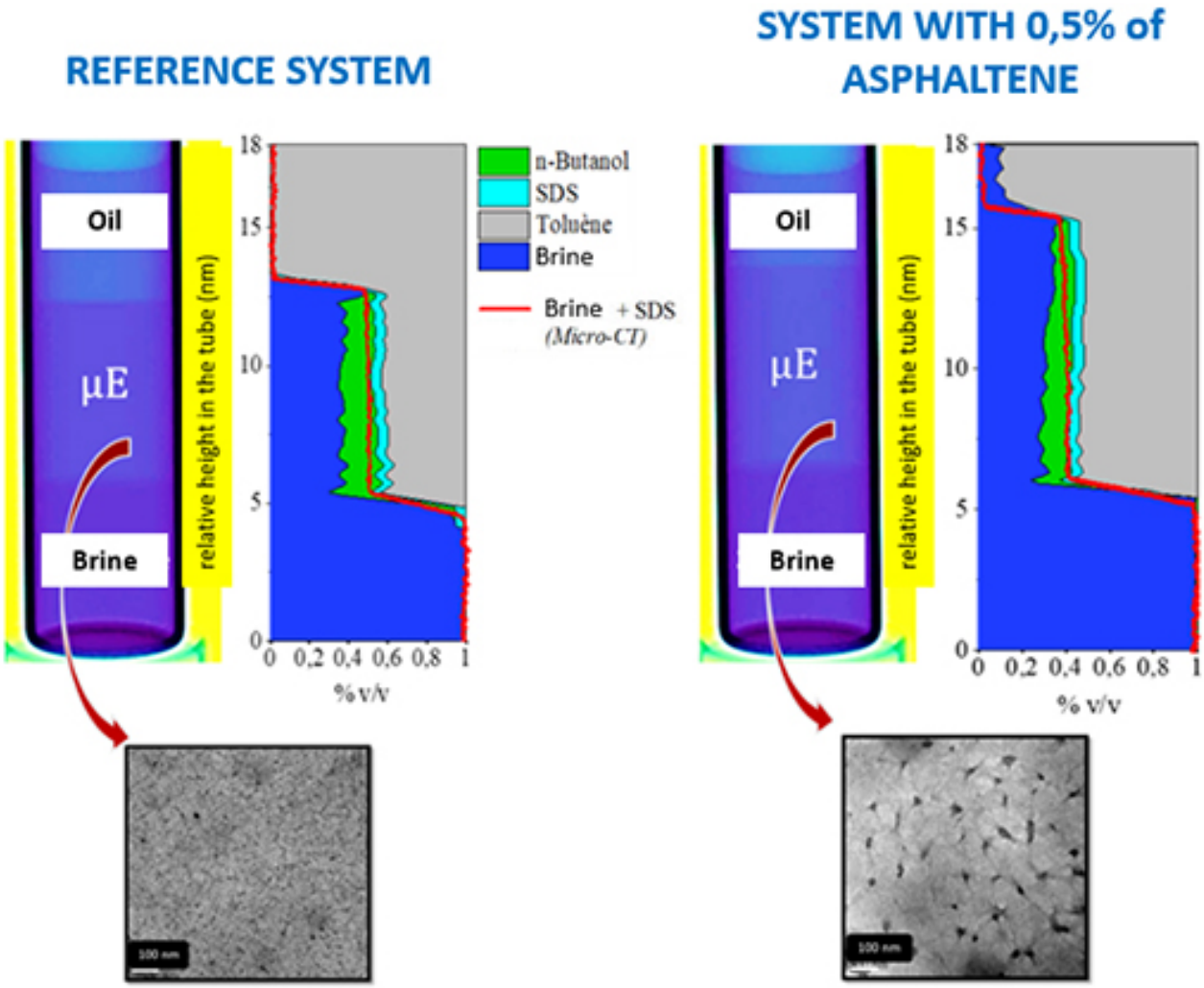

Figure 2: Compositions and thicknesses of the microemulsion phases determined for a model system (brine 54 g/L NaCl/SDS /n-butanol/toluene) and a system with 0.5% asphaltenes. ???Detailed brine, toluene, n-butanol and SDS compositions were determined by NMR. The red curve indicates the brine and SDS surfactant content, determined by X-ray microtomography.
The images present the structure of the microemulsion obtained by cryo-TEM.

The second part of the research involved studying the impact of the presence of asphaltenes on the microemulsion structure further using a combination of techniques: X-ray and neutron scattering (SAXS/SANS), cryo electronic microscopy by transmission (cryo-TEM), DSC[d] microcalorimetry and interfacial rheology measurements using the oscillatory spinning drop method.

In the absence of agitation, and in the presence or otherwise of asphaltenes, the comparison of the results obtained highlighted the transient presence of a semi-crystalline phase during microemulsion formation [2]. In addition, the presence of asphaltenes results in a macroscopic swelling of the bicontinuous phases of the systems observed, a phenomenon that was shown to be correlated with an increase in the size of the microemulsion domains on a microscopic scale. The characteristics of the interfacial film were also determined and appear to indicate that asphaltenes have a significant impact both on its rigidity and also, on a broader scale, on its rheological properties.

A result of significant interest concerning the efficiency of the EOR process is that the presence of asphaltenes does not alter the bicontinuous nature of the microemulsion formed, a key parameter of the process, but simply results in the presence of water in the excess oil phase.

In addition to providing a better understanding of the mechanisms relating to microemulsion formation, this PhD research provided a new experimental methodology, based on a set of robust and complementary techniques, to improve the characterization of their behavior. This advance could be extended to other application contexts involving microemulsions: reaction processes, extraction processes or nanoparticle synthesis.

a- Presenting the same number of carbon atoms
b- NMR: Nuclear Magnetic Resonance, SAXS (Small Angle X-rays Scattering) and DLS (Dynamic Light Scattering)
c- Sodium Dodecyl Sulfate
d- DSC (Differential Scanning Calorimetry).

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