PhD students' day 2024

11th of June 2024

Schedule

9h00 – 9h20 Welcome and Registration

9h20 – 9h30 Welcome Speech

9h30 – 11h00 Oral presentations

9h30 - Feliz-G. - ***New ways of converting biochar into bio-sourced materials with controlled properties***

9h55 - Arias G. - ***High-resolution characterization of bio-oil from catalytic pyrolysis by FTIR, GC-MS and FT-ICR-MS: a comparative study***

10h20 - Edumujeze D. - ***Green Solvent and Catalyst Synergy: Maximizing Furfural Yield from Xylose Dehydration with a Co-Solvent System***

11h00 – 11h30 Coffee Break/Poster Session

11h30 – 12h30 Oral presentations

11h30 - Clément J. - ***Experiments on permafrost blocks in a wave flume***

11h55 - Police S. - ***Green Solvent and Catalyst Synergy: Maximizing Furfural Yield from Xylose Dehydration with a Co-Solvent System***

12h20 – Normandie doc' presentation

12h30 – 14h00 – Lunch break

14h00 – 16h30 – Oral presentations

14h00 – Chakraa H. - ***Algorithms to monitor an industrial area by a team of autonomous mobile robots***

14h25 – Urrea F; - ***Necessary optimality conditions for time optimal control problems in the space of measures***

14h50 – Aglif K. - ***Study of the distribution of chemical elements in zirconia grains and grain boundaries using quantitative Atomic Tomography Probe analyses***

15h15 – Joret M. - ***Second harmonic generation by carbonaceous nanoparticle aerosols***

15h40 – Dongmo R. - ***Study of Structural and Optical Properties of CIGS Photovoltaic Cells***

16h05 – Loweski Feliz M.- ***Valorisation de la biomasse par gazéification pour la production d'hydrogène ou d'électricité sous Aspen plus***

16h30 – 17h00 – Coffee Break/Poster Session

17h00 – 17h30 – Awards ceremony/closing speech

Abstracts

Oral Presentations

Posters

Oral Presentations

New ways of converting biochar into bio-sourced materials with controlled properties.

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Keywords: Biochar, pyrolysis, bio-based materials, characterization.

Biochar is a porous, carbon-rich solid with several remarkable characteristics, such as a high specific surface area, well-structured pores, and an abundance of functional groups. It is obtained by thermochemical treatment of biomass. Its properties vary according to the source biomass and pyrolysis conditions. [1]. Generally, biochar is an economical and versatile material, making it attractive for use as a reinforcement in manufacturing bio-composites. [2]. This research aims to develop new high-performance polymer/biochar blends. The properties of biochar-reinforced polylactic acid (PLA) bio-composites prepared by hot-pressing and extrusion techniques are analyzed. The biochar used is derived from slow pyrolysis at 600°C in a semi-continuous reactor, using two types of biomass: beechwood pellets and Laminaria Digitata seaweed chaff. Elemental and proximal analyses were used to characterize the biomass feedstock. The results show that beech wood has a higher carbon content than seaweed straw, at 46.8% and 33.42%, respectively. Fig. 1 shows that the beechwood biochar (BCBH) has more pores and a more structured pore organization, with distinct shapes for each type of biochar. The thermal properties of the biocomposites were also examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

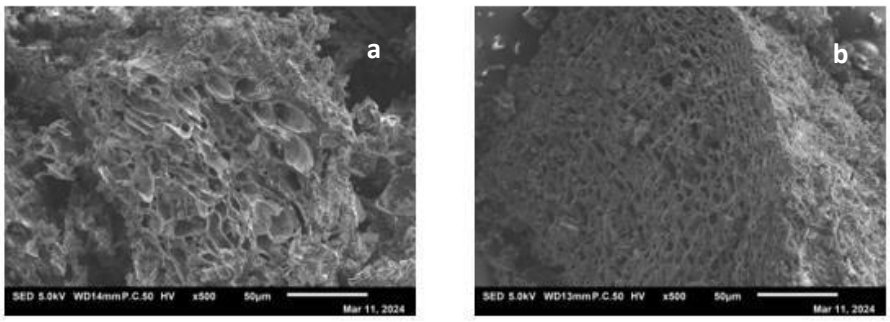

Figure 1:SEM images of biochar prepared from (a) Laminaria Digitata algae, (b) beech wood.

[1] Y. Li, R. Gupta, Q. Zhang, et S. You (2023): **Review of biochar production via crop residue pyrolysis: Development and perspectives**, *Bioresource Technology*, vol. 369, p. 128423, févr. 2023, doi: 10.1016/j.biortech.2022.128423.

[2] K. Aup-Ngoen et M. Noipitak,(2020): **Effect of carbon-rich biochar on mechanical properties of PLA-biochar composites**, *Sustainable Chemistry and Pharmacy*, vol. 15, p. 100204, mars 2020, doi: 10.1016/j.scp.2019.100204.

High-resolution characterization of bio-oil from catalytic pyrolysis by FTIR, GC-MS and FT-ICR-MS: a comparative study.

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KEYWORDS: *Catalytic pyrolysis, Bio-oil characterization, Petroleomic approach.*

Our work aims to study the deoxygenation potential of catalysts on the pyrolysis of biomass. For this purpose, bio-oil was produced from beechwood using zeolite in its commercial form (HZMS-5) and a modified zeolite with a metal loading of 1.4% of iron and nickel (FeNi/ZMS5). The modification was achieved by wetness impregnation and previously studied by our group [3]. A fluidized bed reactor loaded with the catalysts was used to perform the pyrolysis. The resulting bio-oil was characterized using FT-IR, GC-MS and high-resolution FT-ICR-MS with 3 ionization sources (ESI (+), ESI (-) and APCI (+)). Bio-oil produced using sand as fluidized bed was also studied for reference and comparison purposes.

FT-IR spectra shows a decrease in -OH peaks which are attributed to alcohols, carboxylic acids, phenols when catalysts were used. GC-MS provided an insight to the lighter molecules contained in the sample. Catalysts allowed for the identification of more molecules due to its cracking properties. The intensity of oxygenated compounds decreased in comparison to the raw bio-oil. Around 4000 chemical formulas were attributed by FT-ICR-MS with the ESI and APCI in positive ion mode and only around 1000 with ESI in negative mode. Oxygenated compounds with a maximum of 15 oxygens were identified. These attributions show that the bio-oils from catalysts have a similar chemical composition. No molecules for the classes $O_{11}O_{12}$ were identified with ESI (-) for the bio-oil obtained with FeNi/ZMS-5, suggesting the deoxygenation power of the catalyst.

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Green Solvent and Catalyst Synergy: Maximizing Furfural Yield from Xylose Dehydration with a Co-Solvent System

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Keywords: Sustainable green process, biofuel, heterogeneous catalysis

As we gradually recover from the impact of the global COVID-19 pandemic, the world is currently faced with an alarming energy crisis. Our dependency on the use of petroleum and its products as energy source and petrochemicals has led to an ever-increasing climate change and energy poverty. On a global scale, fossil fuel contributes to about 80% of the greenhouse gases. To achieve the Paris agreement and its goals to mitigate the global temperature rise to less than 2°C by 2050, the transition from the dependency of fossil fuel into renewables must be swift and sustainable.

Furfural is a high-value-added molecule which can be obtained from lignocellulosic biomass. Furfural and its derivatives are widely used as transportation fuels, gasoline additives, lubricants, organic solvents, resins, decolorizing agents, flavour enhancer for food, drinks and many other applications. The global market value of furfural was evaluated to about $520 million in 2021 and is expected to reach $817.8 million by the end of 2031.

Commercially, Furfural is produced from the mineral acid dehydration of lignocellulosic biomass with relatively high concentration of hemicellulose. Low furfural yield (<50%), corrosion of equipment and high cost of products-catalyst separation and recovery are some problems associated with the existing industrial process.

Numerous methods have been proposed for the production of furfural from literature with a singular aim of increasing its yield. Due to side degradation reactions occurring concurrently (condensation, fragmentation and resinification) there have been no significant improvement in the process.

Herein we proposed the use of an heterogenous solid catalyst (amberlyst-15) and a bio-based alcohol: co-solvent system for the dehydration reaction. It was observed that the co-solvent system was able to hinder the side reactions, thus promoting high furfural yield (> 70%) at a shorter reaction time (3hr). The inclusion of the co-solvent to the solvent system facilitate faster dehydration of xylose than pure alcohol and reduction in the formation of humins which are able to reduce the catalyst activity and thus hinder its reusability. Fig 1 illustrate pictorially the reduction of the dark humin formation as certain portion of co-solvent was included in the solvent mixture. Fig 2. displays the trend in furfural yield with and without the addition of co-solvent while in Table 1, we compared our result with proposed strategies found in literature. The result confirms that our strategy was superior in terms of furfural yield (75.3%), reaction time (3hr) and amount of catalyst utilized 4:1).

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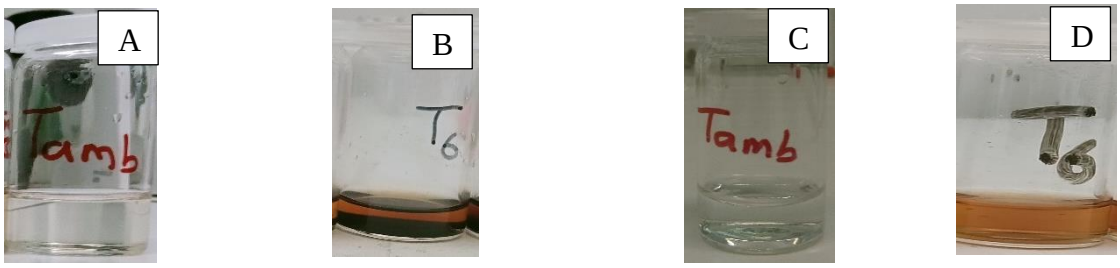

Fig 1. Comparison of humin formation with and with the addition of co-solvent (CS)

[A]Reactive mixture before experiment with 0%CS [C]Reactive mixture before experiment 30%CS

[B]Reactive mixture at the end of reaction with 0%CS [D]Reactive at the of reaction with 30%CS

Table 1. Comparison of performance

CATALYST	SOLVENT	Xylose to Catalyst ratio	REACTION TIME (hours)	FURFURAL YEILLD (%)	REFERENCE
Amberlyst-15	70%ALOH:30%CS	4:1	3	75.2	This work
Amberlyst-15 et Γ-Al_2O_3	DMF	0.003:1	8	46	[1]
Amberlyst-15 et Hydrotalcite	N,N-dimethylformamide	0.5:1	3	51	[2]

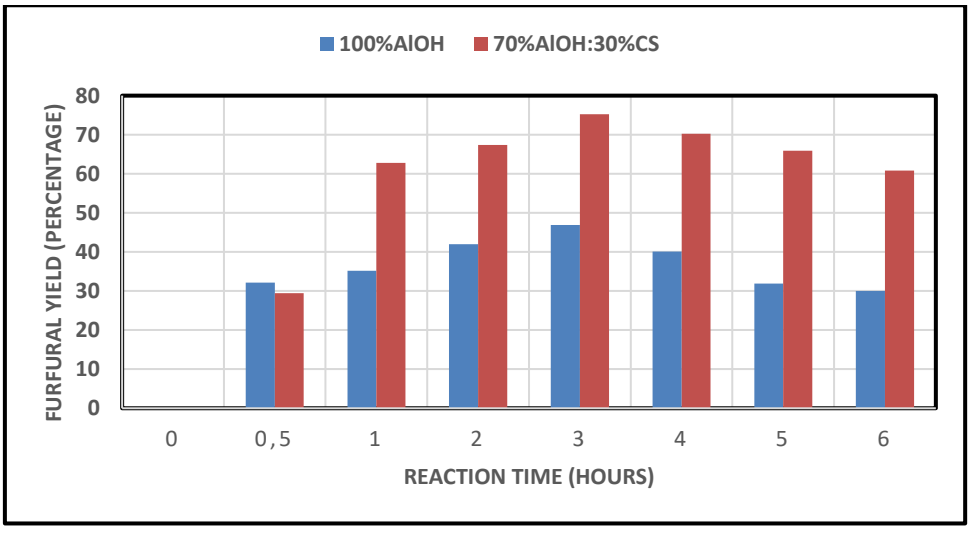

Fig 2. Effect of co-solvent on the furfural yield

Experiments on permafrost blocks in a wave flume

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Keywords: Permafrost, Experiments, Wave flume, Erosion rate, Melting processes.

Permafrost is a ground that remains frozen for at least two consecutive years. It is controlled by the mean average air temperature, so it is found in high latitudes and altitudes [1]. Permafrost has been particularly affected lately by global warming [2]. Its extent is decreasing rapidly, sometimes leading to disastrous consequences, such as landslides or tsunamis [3]. It is an important topic to investigate, as many people and structures are affected by permafrost thawing near coastal areas. Because of the ice mixing with sediments, those coasts are affected by important erosive processes, different from those affecting low latitude coasts [4]. Only a few studies have tried modelling physically permafrost, and even less from a coastal point of view [5].

The purpose of this study is to place permafrost blocks in a wave flume in to assess the wave component in the coastal erosion. Permafrost blocks are created in the M2C cold rooms using box made of pvc. They are 30 cm high and 50 cm wide. A complex protocol has been imagined in order to carry the block into the flume. Only sinusoidal waves have been used for now. While the block is degrading, we monitor it with six instruments: a timelapse camera and a GoPro for the morphological evolution, a thermal camera and iButtons (small thermal sensors) placed inside the block for the thermal evolution, an acoustic Doppler velocimeter and resistive poles for the hydrodynamic evolution. Their purpose is to observe the changes under different experimental conditions (change of wave height, water temperature, sediment type).

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Methodological and operational approaches to the cumulative effects of human activities at sea (CIFRE thesis)

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(Times New Roman, 12, normal, centered, underline presenting author, mark corresponding author with * and enter the email address below, give the affiliations for all authors)

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Keywords: Cumulative effects, English Channel, Marine spatial planning, Methodology

The English Channel-North Sea system is one of the most anthropized maritime zones in the world[1], with a significant accumulation of human activities (fishing, extraction of marine aggregates, submarine cables, offshore wind turbine installation, port dredging and dredging deposits). This multiplication of human activities raises the issue of so-called cumulative effects. Several factors of change can interact with each other, which can have significant consequences on ecosystems. Changes in ecosystems can therefore be attributed to different factors, but also to their interactions. The concept of cumulative effect resulting from the accumulation of multiple factors of change is used in many fields of science and applied in ecology in North America in 1990[2][3]. It was only later that the European scientific community became interested in this subject, notably in the transposition of the European Framework Directive Strategy for the Marine Environment (DCSMM) and with the recognition of the need for a global approach advocating the ecosystemic. In France, article R122-5 of the environmental code specifies that impact studies must deal with the 'cumulation of impacts with other existing or approved projects (…)'. In this legislative framework, the development of a methodology for evaluating cumulative effects is a current issue shared by all project leaders subject to impact studies, in order to be able to build the 'cumulative effects' chapter of these studies. On the Eastern Channel - North Sea front, sea project leaders, as well as CRPMEM Normandie and the Universities of Caen, Rouen and Le Havre, have grouped together within the framework of the Scientific Interest Group 'Cumulative Effects at Sea' (GIS ECUME), with the objective of acquiring knowledge on the cumulative effects of human activities in coastal environments. The objective of the thesis is the implementation of a methodology for evaluating cumulative effects, intended to feed the impact studies of human activities at sea.

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Algorithms to monitor an industrial area by a team of autonomous mobile robots

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Abstract: Recently, considerable attention has focused on enhancing the security and safety of industries with high-risk activities to protect equipment and the environment. Chemical processes and nuclear power generation, in particular, can have significant impacts on their surroundings. In major events such as chemical spills, oil rig explosions, or nuclear accidents, collecting accurate and rapidly evolving data becomes a challenging task. Coordinating a fleet of autonomous mobile robots is a promising way to handle unexpected events and prevent malicious actions. This presentation addresses the problem of optimally assigning a set of tasks to a set of mobile robots equipped with different sensors to minimize a global objective function. The robots perform sensing tasks to monitor the area and assist firefighters and inspectors during a disaster by providing necessary measurements. For this purpose, a centralized Genetic Algorithm (GA) is proposed to determine the tasks each robot will perform and their order of execution. Additionally, we focus on the task routing aspect to improve the computed solution using the 2-Opt local search method. The proposed approaches are tested through a simulation scenario of a grid map environment representing an industrial area of the city of Le Havre, France. Furthermore, a comparative study is conducted with the Hybrid Filtered Beam Search (HFBS) approach and the Mixed-Integer Linear Programming (MILP) solver CPLEX. The results demonstrate that the GA-based approach offers a favorable balance between optimality and execution time. Experimental validation with a team of drones is also presented.

Keywords: Multi-robot systems (MRS), multi-robot task allocation (MRTA), optimisation, industrial monitoring.

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Necessary optimality conditions for time optimal control problems in the space of measures.

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Keywords: Optimal control – Continuity equation - Wasserstein spaces – Pontryagin maximum principle

We are interested in developing necessary optimality conditions in the form of a Pontryagin maximum principle ([1]) for the minimal time Bolza optimal control problem with constraints in the final time. In this problem the dynamic is given by a non-local continuity equation in the Wasserstein space of probability measures, the set of controls are taken in open-loop form and the set of constraints is represented by functional inequalities applied to the terminal time. To this end, we relate the main challenges of this problem from which a fair amount is accounted by the fact that Wasserstein spaces are not Banach and its difficulties on defining differentiability ([2],[3]).

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Study of the distribution of chemical elements in zirconia grains and grain boundaries using quantitative Atomic Tomography Probe analyses

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Keywords: M5Framatome; Atom probe tomography; Zirconia; Corrosion

The integrity of fuel rod cladding in Pressurized Water Reactors (PWRs) is critical for containing fission products. Zr-based alloys are commonly used for cladding due to their favorable mechanical properties and neutron transparency. However, these alloys are susceptible to corrosion, especially oxidation and hydriding, posing significant safety and performance challenges. B. Queylat's thesis utilized Secondary Ion Mass Spectrometry (SIMS) to analyze oxide layers on M5Framatome alloy under PWR conditions. His research identified a depletion of Nb near the oxide/metal interface, suggesting Nb rejection from oxygen-enriched areas, which is linked to hydrogen uptake and hydriding [1]. To thoroughly understand the oxidation and hydrogen absorption mechanisms in M5Framatome, a detailed study of Nb redistribution is necessary, achievable only through Atom Probe Tomography (APT) due to the small size of the oxide grains.

Our research objectives are twofold: optimizing APT experimental parameters for enhanced accuracy and reliability, and investigating Nb distribution and quantifying its local concentration in the oxide layer. We studied thermal oxides formed on a quasi-pure Zr reference material and the M5Framatome alloy to compare mass spectra of zirconia with and without alloying elements. Needle-shaped samples were prepared using Scanning Electron Microscope coupled with Focused Ion Beam (SEM-FIB) and analyzed in laser mode to minimize electrostatic stress [2].

A parametric study on the influence of laser frequency, base temperature, and laser energy on the oxygen fraction was conducted. Results showed preferential Zr evaporation at low laser energies and thermal tails at high laser energies, complicating Nb quantification. Base temperature had minimal impact on mass spectrum quality but affected spatial resolution and success yield, necessitating a compromise. Optimal parameters were determined for APT characterization of zirconia. Python scripts are being developed for accurate quantification using a deconvolution algorithm to mitigate thermal tail effects [3]. Initial results indicate a Nb concentration in the oxide layer of 0.26 at.% (relative to Zr atoms), aligning with the Nb content in the metal solution [4].

This study enhances the understanding of APT evaporation mechanisms for accurate alloying element quantification in zirconia. Future work will investigate the role of Nb distribution in oxidation and hydriding processes.

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Second harmonic generation by carbonaceous nanoparticle aerosols

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Keywords: Black carbon, Second harmonic generation (SHG), non-linear optics, Aerosol

In the present study the second harmonic generation (SHG) by black carbon particles, also named soot, is quantified an analysed.

SHG is a non-linear optical (NLO) phenomenon that is typically used in biosciences and fundamental physics and has shown to have large potential for the investigation of surface sensitive phenomena. While well known in applications on particles in solution or nanoparticles located on the surface of droplets, the SHG by black carbon particles in aerosol phase themselves has not been demonstrated yet. The present work aims at narrowing this gap by exposing a jet of well-defined soot particles by a femtosecond laser featuring high peak pulse energies allowing to induce NLO phenomena. The experiments are carried out in an innovative optical setup allowing to analyse the NLO response resolved in time, wavelength and angle, thus having the capability to isolate SHG from other phenomena, such as laser filamentation. The optical setup was calibrated in order to quantify the generated energy and optimised in order to have a high signal sensitivity and in order to avoid NLO generation from its own optical elements.

The results confirm that soot particles feature SHG at intensities that are more than 7 orders of magnitude smaller than that of linear light scattering. SHG increases with particle size, however the link with particle surface seems to be more complex. SHG is also giving different angular signatures at particles with different graphitic content, which could indicate that the phenomenon is driven by symmetry breaking on the particle surface.

With the importance of composition related phenomena associated with black carbon, these results can give way to a new class of diagnostics for analysing the evolution of these particles.

Study of Structural and Optical Properties of CIGS Photovoltaic Cells

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Keywords: CIGS, solar cell, cathodoluminescence, tandem

The selenide CIGS (Cu(In1-xGax)Se2) is the most efficient thin-film solar cell, with a power conversion efficiency of 23.4%. However, achieving higher efficiencies is limited by the Shockley-Queisser limit, which sets the maximum efficiency for a single-junction solar cell at 33%. This has led to the development of tandem solar cells. Pure sulphide CIGS (Cu(In1xGax)S2) is an ideal candidate for the top cell in a tandem configuration with silicon solar cell (as a bottom cell) due to its adjustable band gap ranging from 1.5 eV (CuInS2) to 2.4 eV (CuGaS2) [1]. Incorporating sodium into CIGS, which can enhance performance, can be done before, during, or after layer growth. Additionally, molybdenum as a back contact facilitates the migration of sodium from the substrate to the CIGS layer [2].

Our study aims to investigate, firstly, the structural properties of four differently sodium-treated CIGS films using X-ray diffraction (XRD) and, secondly, the optical properties of these samples using Cathodoluminescence (CL). This technique enables us to characterize the band structure of our layers. XRD patterns reveal that all four CIGS layers (for our four samples) have grown in a single chalcopyrite phase. Additionally, utilizing Vegard's Law, we determined GGI, which was confirmed by CL spectra. We also observed that sodium posttreatment helps eliminate defects within the bandgap as shown in figure 1. Finally, post-treated layers exhibit a larger bandgap grading, enhancing the electronic properties of the solar cell.

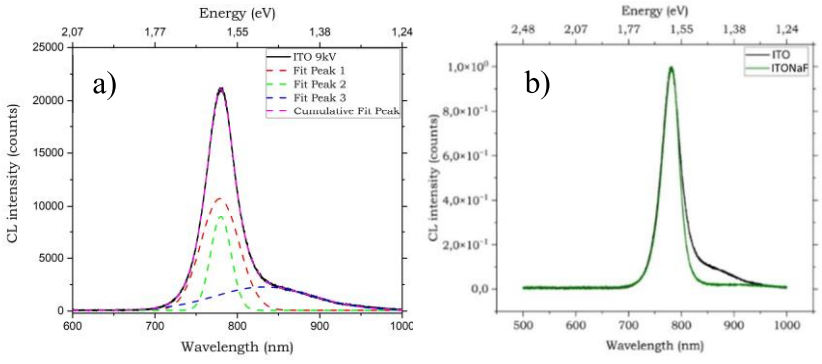

Figure 1: a) CL spectrum of the ITO sample (without NaF treatment) obtained at 9kV, b) normalized and superimposed spectra of the ITO and ITONaF samples (with NaF treatment).

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Valorisation de la biomasse par gazéification pour la production d'hydrogène ou d'électricité sous Aspen plus

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Keywords : Simulation, gazéification, hydrogène, électricité.

La demande croissante d'énergie et l'épuisement continu des combustibles fossiles incitent à trouver de nouvelles sources d'énergie renouvelables susceptibles de satisfaire une grande partie des besoins énergétiques et de réduire les problèmes de réchauffement de la planète. Cette étude présente une simulation du procédé de gazéification de la biomasse selon deux voies de valorisation, la production d'hydrogène et la production d'électricité.

La première étape considérée pour la simulation est le prétraitement de la biomasse incluant le séchage et le broyage. L'étape de gazéification utilise un réacteur à lit fluidisé simulé à l'aide de corrélations en fonction de la température provenant de résultats expérimentaux obtenus par notre équipe [1], [2]. Afin d'optimiser la production d'hydrogène, trois étapes clés des réactions catalytiques ont été simulées. La première étape consiste à réduire les goudrons par craquage catalytique en utilisant du biocharbon comme catalyseur. Cette étape est simulée à l'aide d'une cinétique spécifique. Par la suite, le gaz produit passe dans un réacteur de reformage catalytique à la vapeur dans lequel une cinétique de type Langmuir-Hinshelwood-Hougen-Watson (LHHW) est appliquée. La dernière étape est la réaction Water-Gas Shift (WGS), également simulée avec des cinétiques.

Après l'étape de gazéification, le procédé de production d'électricité est simulé à partir d'un réacteur de combustion qui augmente le pouvoir calorifique du gaz de synthèse. Ce gaz de combustion est ensuite utilisé afin de générer de la chaleur alimentant une turbine à vapeur, produisant de l'électricité.

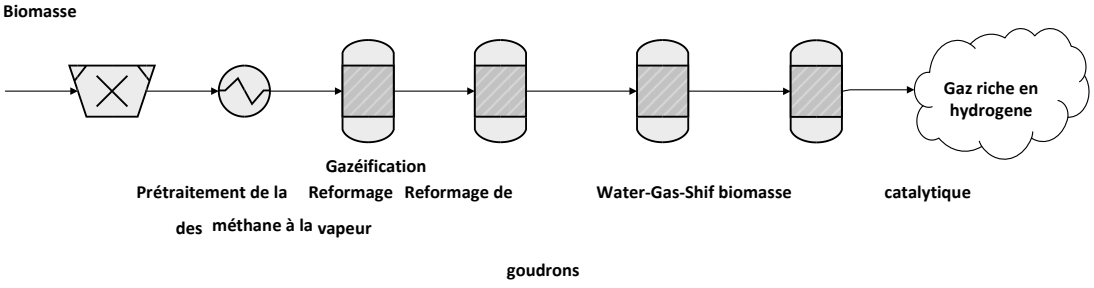

Fig. 1. Schéma de l'installation de production d'H2 par gazéification de la biomasse

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Posters

Microscopic behaviour of hydrogen and hydride Molecules in Atom Probe Tomography of Zirconium

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Keywords: Hydrogen - Zirconium – Hydrides - Field

The understanding of Zirconium (Zr) and Hydrogen (H) interactions is a topic of interest in the field of materials science. Zr is known to have a strong affinity with hydrogen, which can lead to the formation of hydrides that can affect the mechanical properties (embrittlement, cracking, etc) of the material [1]. Our studies are carried out on pure Zr analysed by laser-assisted atom probe tomography. This is complex, because the hydrogen detected during the analysis could come from the analysis chamber (parasitic hydrogen) or from the material (hydrogen contained in the material). Our results show the formation of hydrogen species H^+, H_2^+, H_3^+ and hydrides ZrH_x^{2+}. The evolution of the relative abundances of H^+, H_2^+, H_3^+ depends on the surface field estimated from the Zr^{3+}/Zr^{2+} ratios, as seen in previous studies on other materials[2]. This is not the case for the hydrides which overlap with the Zr isotopic species. In this contribution we will discuss the quantification of hydrogen and zirconium hydrides, their localization inside the material and their dependence on the field.

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Two-line laser induced fluorescence of indium to study flame-wall interactions

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Keywords: thermometry, laser induced fluorescence, indium, flame-wall interactions, combustion

During the last two decades, global air traffic has sharply increased and in 2022, the aviation industry was responsible for 2% of total CO2 emissions [1]. Radical changes are needed to reach net zero emissions by 2050. To do so, several solutions are considered and among them, replacing conventional fuels by hydrogen seems promising [2].

Producing no carbon-based emissions, hydrogen combustion is characterized by fundamentally different properties. Because of this, combustion chamber architecture has to be entirely revised, especially in the near-wall zone, which is subject to important thermal fluxes. It is necessary to enhance our understanding on flame-wall interactions, term referring to all the coupled processes between the reactive flow (heat transfers, temperatures, chemical composition) and the material (mechanical properties, role of the manufacturing process).

The aim of this study is to implement a laser-based diagnostic to perform temperature measurements on academic installations and hence, clarify the role of temperature during flame-wall interaction processes. Two-line atomic fluorescence is the chosen technique: the population of two lower lying electronic states of a seeded atom, for example indium because it is a suitable marker for flame temperatures (above 1000 K) [3], are probed and the ratio of the resulting fluorescence is proportional to the temperature [3]. In addition to its non-intrusive feature, its main advantage for a near-wall combustion application is the use of a seeded tracer. Indeed, a method developed by Whiddon et al. [4] using tri-methyl-indium allows to seed atomic indium in all the zone of interest: in the burnt gases as well as in the fresh gases.

The new thermometry platform AURYGA (Atomic fluorescence platform for thermometry in gases) is being developed at CORIA for this study. During a first stage, a reference flame will be seeded (premixed methane/air) with tri-methyl-indium. A calibration of the technique will be performed before implementation on the THOR (Thermal aggression bench to study flame-wall interaction) bench of CORIA. A characterization of the used diode lasers as well as an estimation of uncertainties are planned during this first stage.

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Évaluation de mesures d'accord sur des structures relationnelles par la dégradation contrôlée d'annotations

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Keywords: annotation of relational structures, inter-coder agreement, argumentation analysis, evaluation.

Text corpora are invaluable data sets for scientific research. Already essential for experimental approaches, their interest has grown even more in recent decades with the advances on machine learning. Yet, for these datasets to be usable in the training, and evaluation, of supervised and semi-supervised learning systems, they need to undergo an additional annotation stage [1]. Inter-coder agreement measures are essential for assessing the quality of human annotations on those corpora. In the context of relational structures, however, the question of the quality and interpretability of these measures remains open. This article presents the adaptation of a tool already used for other annotation paradigms. Its aim is to generate erroneous artificial annotations in a controlled manner. The resulting annotations are provided to agreement measures adapted to relational structures, allowing the identification of the behaviour of the measures as well as the differences between them.

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Méta-modèles pour la caractérisation de la réponse stochastique des systèmes mécaniques en rotation.

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Mots clés: *structures en rotation, systèmes variant dans le temps, processus stochastiques instationnaires, propagation d'incertitudes, méta-modèles*

On vise à développer de nouvelles méthodologies pour le dimensionnement des systèmes mécaniques, en tenant compte des phénomènes aléatoires. Nous nous concentrons sur trois objectifs spécifiques : premièrement, l'étude approfondie des systèmes mécaniques pour mieux comprendre leurs comportements [FRI10, HAR16, SAN19]; deuxièmement, le développement de méta-modèles spécifiquement conçus pour quantifier les incertitudes dans les systèmes structurels, comme dans les références [BAE19, CHA21, SUD12, SOU15, SAM18]; et enfin, si le temps le permet, l'analyse de sensibilité pour évaluer l'impact des variabilités et des incertitudes sur les modèles, en combinant approches théoriques et numériques. Cette recherche vise à optimiser le dimensionnement des systèmes mécaniques en présence d'incertitudes, améliorant ainsi leur efficacité et leur performance.

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Couplage de la microfluidique de gouttes et de la microscopie à génération de seconde harmonique pour le criblage in situ de phases cristallines

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Keywords: Droplet Microfluidics, Nonlinear Optics, Crystallization

Le criblage des différentes phases cristallines d'une molécule est essentiel, notamment pour l'industrie pharmaceutique, chacune ayant ses propriétés propres (biodisponibilité, solubilité, etc). Il consiste à utiliser différentes conditions de cristallisation (Température, solvants, sursaturation …) et à observer la phase cristalline qui en résulte. Cette opération nécessite généralement une quantité de produit et un nombre d'essais important [1].

La microfluidique de goutte (µFG) représente une technique de choix pour réaliser ce criblage. En effet, la génération de nombreuses gouttes semblables à de microréacteurs indépendants permet la réalisation d'études statistiques pour des conditions données en un temps réduit. De plus, le volume de ces gouttes (à l'échelle du nanolitre) réduit drastiquement la quantité de produit requise. Enfin, cette technique peut permettre l'obtention de phases cristallines métastables non accessibles par des voies plus « classiques » [2]. La caractérisation des cristaux formés dans les gouttes implique généralement leur extraction et leur collecte donc une analyse ex situ et peut se révéler complexe. Il est préférable d'opter pour une caractérisation in situ des cristaux. L'analyse Raman est souvent choisie mais elle requiert un temps d'analyse important pour chaque cristal (plusieurs minutes/heures par cristal) [3].

Un nouveau couplage est proposé ici entre µFG et microscopie SHG (Génération de Seconde Harmonique). Cette technique d'optique non-linéaire permet de distinguer les structures noncentrosymétriques (signal SHG) de celles centrosymétriques (pas de signal SHG) [4] avec un temps d'analyse réduit à quelques secondes/goutte. Nous montrerons que ce couplage est particulièrement adapté à l'étude de composés présentant des phases stables et métastables différentiables par SHG et qu'il permet un criblage rapide des conditions de cristallisation pour l'obtention d'une forme spécifique.

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Salt screening of racemic Ibuprofen with inorganic bases.

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Keywords: Salt screening, Crystallization, Ibuprofen, Solubility.

Active pharmaceutical ingredients (APIs) are commonly administered to patients as solid-state formulations, which offer stability and compactness, with a convenient format of delivery. The production of APIs in various solid forms, such as single components (e.g., metastable and amorphous phases) or multicomponent systems (e.g., solvates, co-crystals, or salts), yields distinct physicochemical properties. These properties significantly impact the drug's bioavailability, manufacturability, solubility, and stability, thus influencing its overall performance in pharmaceutical processes.[1] Subsequently, salt formation has become a prevalent technique for ionizable compounds in pharmaceutical development. Despite over 50% of approved APIs being marketed in their salt form, [2] challenges persist in the industry to achieve the desired results within the time limitation enforced in industry. Therefore, this work aims at creating an experimental database serving as a tool to aid industrial professionals in their salt screening process. The initial phase focuses on the case of racemic Ibuprofen. It was firstly selected because of its global commercial significance [3, 4] and extensive literature on reported salt formations (e.g., with sodium, lysine, and arginine) [3, 4]. Three inorganic counterions: Calcium, Magnesium and Potassium ions where selected for salt formation experiment. Without any: time, solvent or synthetic method restriction, promising results had been observed, including system with multiple salts and particular solubility behavior. Parameters such as crystalline structure, solubility, hygroscopicity, and thermal stability are studied to provide a comprehensive overview of the obtained salts. The same methodology will be extended to other APIs (e.g., Clopidogrel, Zolpidem, Ketoprofen, etc.) and counterions broadening the database with a diverse array of data points.

Through systematic experiment and analysis, this study aims to facilitate the decision-making in pharmaceutical salt screening processes.

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2D imaging combination of planar optode and DET 2D : application in *Zostera marina* seagrass

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Keywords: seagrass – biogeochemistry – planar optode – gel DET 2D

Seagrasses are marine plants we can find in coastal habitats worldwide. During the 20th century, zosteras meadows have been fragilized by anthropogenic and climatic threats and thus have declined. However, this species is of great interest to preserve the coastline from erosion (sediment stabilization), to filter water, and to maintain the environment's biodiversity (breeding and nursery area for marine fauna, feeding area for marine birds) [1]. A lot of studies focused on the aerial part of the plant, the leaves, but only a few talks about rhizomes [2][3]. Underground interactions are crucial to fully understand the species dynamics and to be able to determine why in some areas seagrasses are declining while elsewhere they are recovering. To do this, we aimed to combine two imaging methods, DET 2D hydrogels [4] and planar optodes [5], in order to better know biogeochemical fluxes between rhizomes and sediment in two dimensions and at least at a millimeter level.

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A new method to describe the vertical zonation of seaweeds on the North-Atlantic shores using a mean sea level index

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Keywords: Macroalgae, Tidal range, Intertidal, Seaweed communities, Vertical distribution

Coastal communities, at the interface of land and sea, face several threats, that can impact the composition, productivity and functioning. In the context of the Water Framework Directive (Directive 2000/60/EC), and the Marine Strategy Framework Directive (Directive 2008/56/EC), macroalgal communities are a recognized tools for the ecological state assessment of coastal waters. Seaweed zonation is traditionally described as the succession of several seaweed belts, that are characteristic of a given bathymetric range, and dominated by 1 - 2 characteristic brown macroalgae. However, this zonation is highly variable between sites due to the varied environmental and anthropological conditions impacting seaweeds. One of the most important factor is tide (and tidal range).

Few studies have focused on the vertical distribution of seaweeds, and the comparison of this distribution across a geographical range. In this study, we selected three sites in Brittany and Normandy, exhibiting different tidal ranges, ranging from 5.5 m to 10 m. Apart from tide, all sites share common characteristics, with extensive rocky substrata and significant seaweed covers. Nine species of brown seaweeds, were targeted. In each site, the seaweed individuals were sampled by foot at low tide, and precisely positioned using a GNSS (SparkFun Facette RTK GNSS) with CentipedeRTK NTRIP correction. The heigh from ellipsoid measured in situ with the GNSS was converted into the heigh from chart datum, and heigh from the mean sea level (MSL). The latter was normalized into a -1 to 1 relative heigh scale.

When comparing the species heigh across the three sites, the range colonized by seaweeds was higher in the high tidal range site. When using the relative heigh, all species shared broadly similar heigh range, with high shore species developing higher than 0.2, medium shore developing around 0.2 and -0.4, and low shore species down to -0.8. However, the distribution of seaweeds reached lower values in the high tidal range site comparatively with the two others, with values reaching -1.1.

Used on a larger scale, this index will help to understand the vertical distribution of species along a longitudinal scale. Moreover, it will be used together with morphometric indices in prediction models to estimate species repartition at large scale.

Translaminar fracture behavior of hybrid woven-ply PEEK thermoplastic laminates under isothermal and kerosene flame exposure

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Keywords: Thermoplastic composite; Translaminar fracture; High temperature; Kerosene flame

With regard to the stringent fire safety regulations for thermoplastic-based (TP) composites in aeronautics field [1], it is a critical issue to understand and quantify the fracture mechanisms of degraded laminates, whose behavior is highly heterogeneous and anisotropic. To date, most attention has been given to unidirectional (UD) thermosetting laminates [2-3]. Therefore, this study aims at investigating the influence of different critical thermal conditions (resulting in the decomposition of the polymer matrix) on both the thermally-induced damages and the fracture behavior of hybrid woven-ply carbon/glass fibers reinforced PolyEther Ether Ketone (CG/PEEK) laminates, as a function of heating temperature and fire exposure time.

Compact Tensile (CT) specimens are exposed to isothermal (melting temperature 350°C to the decomposition temperature of matrix 550°C by a high temperature furnace, for 15 min) and one-side kerosene flame (characterized by a heat flux of 116 kW/m^2 and a temperature of 1150°C by a burner bench, from 5 min to 15 min) exposure conditions. Tensile tests are then conducted to assess the mode I translaminar fracture toughness at room temperature. Crack propagation is measured during mechanical loading using a Digital Image Correlation (DIC) device combined with a binarization algorithm [2]. Then, the G-R curves have been obtained from the compliance method during crack propagation [3].

In the isothermal case, the residual mechanical properties degrade with increasing heating temperature, particularly once thermal decomposition is about to start, due to the formation of porosities and extensive delamination. Under the kerosene flame exposure, the microscopic and tomographic observations reveal thermally and mechanically induced damages with a heterogeneous distribution due to temperature gradients. Depending on the pyrolysis degree of each ply, the structural capacities of the plies gradually deteriorate from the exposed to the opposed side. The translaminar fracture toughness tends to slightly increase during crack propagation, whereas the structural capabilities of CG/PEEK laminates decrease with the increasing flame exposure time, as secondary cracks within the char region may prevent the compliance method to be applied.

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Improved Double Deep Q – Learning Approach for Voltage Control of Buck Converter

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Keywords: Buck Converter, Deep Q – network, PI

Buck converter, a popular non-linear DC/DC converter, reduces a higher DC voltage to a lower level for various applications, such as in DC microgrids, electric vehicles, and electronic devices. Maintaining a stable output voltage requires precise closed-loop control, as the converter is sensitive to unpredictable input voltage variations, disturbances, and variable load conditions. These challenges are further amplified by the negative impedance effect of constant power loads (CPLs), where even small voltage fluctuations can be amplified into uncontrolled voltage swings [1]. Therefore, a critical robust and fast-acting control strategy is essential for efficient voltage regulation. Model-based controllers such as PI has been employed for voltage regulation, however, their performance is heavily influenced by the accuracy of the mathematical model of the converter, any unmodeled dynamics and uncertainties can hinder its effectiveness [2]. Furthermore, any dynamic changes within the converter itself, such as those resulting from aging or replacement of worn-out components, might necessitate re-tuning for improved performance. To address these challenges this paper presents an improved double deep Q-network (DDQN) controller that utilizes deep neural networks to learn the optimal duty cycle based on the current state of the converter without the needs of its detailed mathematical model. Firstly, the improved DDQN achieves stability through well-defined observation parameters and an appropriate reward/penalty function. Secondly, tuning of the agent's hyperparameters was carried out to realize robust controller. The proposed controller was simulated and tested in Matlab/Simulink environment under different input voltage and variable load conditions. The simulation results in Figure 1 demonstrate better transient response and robustness against varying load conditions compared to PI controller.

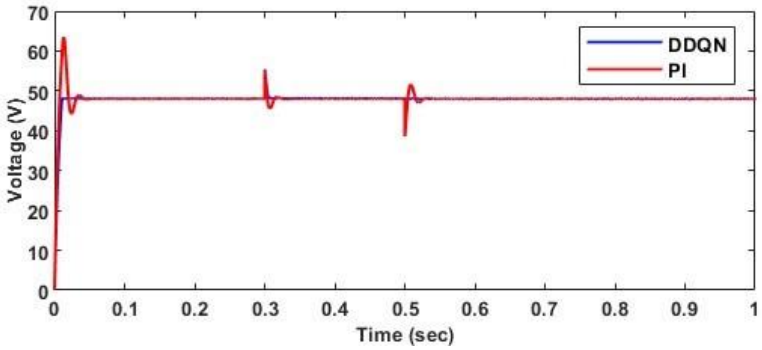

Figure 1: Voltage Response using DDQN & PI Control under Varying Load Conditions

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Test Protocol Development for Electric Vehicle Fast Charging

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Keywords: Lithium-ion batteries, fast charging, ageing test

The successful integration of the EVs system in the market largely depends on the battery technology used. Lithium-ion batteries are widely used in the EVs due to their performance, such as high energy, power density, and lifespan. However long charging time compared to the refueling ability of the conventional ICE vehicles hinder their wider acceptation [1]. There are a lot of concerns with regards to the fast charging of the lithium-ion batteries which include, among others accelerating aging factors, the temperature rising and the dendrites' formation [2] [3]. Thus, an appropriate fast charging strategy to achieve a compromise between charging time and battery lifetime is the current challenge.

In this study, pulse charging technique is studied by investigating the sensitivity of its control parameters. Therefore, different charging conditions are established through combination of three different duty cycles (α) and frequencies in the range of 1 Hz to 0.01Hz. In each condition, three cells are sampled and charged with the positive pulse charging strategy characterized by a 3C current value, at the selected duty cycles (α) of 33.3%, 50%, and 66.6%, respectively. Performance of the fast charging is evaluated by comparing results obtained during the pulse test with ones obtained in nominal CC charge. Li-ion batteries with $LiFePO_4$/graphite (LFP/G) electrode materials are used in this research. Results' analysis showed that the 33.3% duty cycle has a similar behavior to the CC charge. Consistent time reduction is observed by increasing the duty cycle to 50% and 66.6%. Moreover, both battery capacity and charge/discharge efficiency are respected. However, the heat generation increased with (α) causing a higher temperature rise. As a consequence, a suited cooling system (regulation) is recommended. Finally, results are analyzed to find the optimal parameters for pulse charging. This allowed the long-terms ageing tests protocol set-up for ageing characterization.

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AI-enabled radiotherapy quality assurance in clinical trials

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Keywords: AI, Radiotherapy, Clinical Trials, Medical Imaging

Radiotherapy is a means of treating cancer by irradiating the cancer cells with nuclear particles. Radiotherapy planning involves several steps in which tumour and healthy organs are delineated on a CT scan, dose map is simulated, and irradiation machine parameters are specified. Patients' outcomes may be enforced by radiotherapy quality assurance (RTQA). A particular process in RTQA in clinical trials is individual case review (ICR) in which radiation oncologists and medical physicists evaluate delineations and dose map on the CT scan based on a predetermined protocol of the clinical trial. Low quality of CT scan may hinder evaluation by the referring oncologists and the medical physicists. Quality of CT scans may suffer from the presence of metals, patient movement, wrong choice of CT scanner protocol, noise, low pixel resolution, focal spot (where electrons hit to create the beam) size and slice thickness. In this project, an image restoration algorithm from generative AI is investigated after the degradations significant for ICR are simulated computationally. To rank images in the dataset according to their quality, LIQE[1] and BRISQUE[2] algorithms are evaluated on a CT scan slice with its resized and Gaussian noise-added versions as well as comparing that slice to a slice right next to it with metal artefact. For metal artefacts, a way to simulate metal artefacts on clean CT scans is used[3]. For noise, local variance map is used to simulate realistic CT noise by CIL library[4]. For low pixel resolution, bicubic resizing is applied. For slice thickness, weighted average[5] is taken. For metal artefact simulation Feldkamp, Davis, and Kress (FDK)[6] filtered back projection is required. Ram-lak, Shepp-Logan, Cosine, Hamming, Hann and a Custom Ram-Lak(Ram-Lak filter multiplied by 1.04) for FDK are compared for fidelity to the original image[4]. To improve the quality of ground truths two computations are explored: ring removal and centre of rotation correction[4]. Mean absolute error (MAE) is measured for those comparisons. BRISQUE gave 131.4826, 114.7502, 153.5910, 89.0656 and LIQE gave 1.1897, 1.1212, 1.0560, 1.0887 for clean, with metal artefact, lowered resolution, and noise-added versions of the same image. Lower is better for BRISQUE and higher is better for LIQE. BRISQUE failed to give lower score for degradations of metal artefacts and noise meanwhile LIQE detected all the degradations. MAEs were 15.696573, 15.871427, 16.3526, 16.877684, 17.010777, 12.44884for Ram-lak, Shepp-Logan, Cosine, Hamming, Hannand a custom Ram-Lak. Centre of rotation correction decreased MAE from 15.696573to 15.696262. Ring removal left artefacts on the scan while still maintaining the same MAE of 15.7. LIQE proved to be a good tool to measure CT degradations important in ICR. Ring removal and centre of rotation didn't contribute any noticeable improvement for ICR but ring removal caused obstructing artefacts on the scan. The custom filter gave the most fiducial reconstruction.

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Experimental and numerical study of the chemical behavior of the ternary $CoSO_4$-Li_2SO_4-H_2O system

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Keywords: Solubility, phase diagram, Modeling, $CoSO_4$, Li_2SO_4

Cobalt sulfate and lithium sulfate are two of the main compounds obtained from the recycling of Lithium-ion batteries (LiB). Leaching is used to extract metals from the used batteries, but these methods require: i) high quantity of solvent and ii) expensive costs for neutralizing the acid. Multiple alternative recycling methods have already been proposed [1], but the cost is still too high compared to extracting raw materials [2].
The improvement of previous methods or the development of new alternative methods for recycling LiB after leaching require an improved knowledge of the physicochemical properties of these solutions and a better understanding of their chemical behavior. The approach adopted in this study combines thermodynamic modelling, based on the Pitzer model [3], and experimental data acquisition. Thus, new experimental thermodynamic data, such as solubilities, heat capacities and osmotic coefficient have been measured to help developing a reliable thermodynamic model for the $CoSO_4$-Li_2SO_4-H_2O system.
During this study, solubilities have been determined by Discontinuous Isoperibolic Thermal Analysis (DITA) [4]. Dynamic Vapor Sorption (DVS) experiments were carried out to characterize hydrated solid forms and to obtain osmotic coefficients. Calorimetric measurements have been performed to obtain heat capacities of $CoSO_4$ and Li_2SO_4 aqueous solutions. InSitu-X-Ray Diffraction measurements (InSituX®) [5] were used to describe and characterize the rich landscape of hydrates of the binary phase diagram $CoSO_4$–H_2O.
All these experimental data contribute to the calibration of the Pitzer model, i.e. the determination of the specific interaction parameters between solutes. In a first step, the binary cation-anion parameters are determined allowing description of the osmotic coefficient of both binary systems. In a second step, ternary interaction parameters are optimized to calculate the salt-solution equilibria in the ternary phase diagram $CoSO_4Li_2SO_4$-H_2O. The temperatures we investigated so far range from 10°C to 50°C.

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An Helmoltz-Hodge decomposition in the Wasserstein space

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Keywords: Hodge decomposition, Wasserstein, Solenoidal fields

The Helmoltz-Hodge decomposition states that any sufficiently regular vector field f is uniquely given by $\text{grad}(g)+h$, where h is divergence-free. Extensions to the L^2 setting are known since the early 1960's, and rely on the Hilbertian geometry of vector fields [1].

This poster presents an extension of these results whenever the f to be decomposed is no longer a vector field, but a *measure field*, i.e. may give a probability to different vectors at each point. The recent development of the Wasserstein geometry [2] provides the correct generalization of the L^2 setting. It is shown that any measure fields decomposes in an unique way in two components that are orthogonal in some sense, and support the same gradient/divergence-free interpretation. However, some properties are lost with respect to the vector field setting: to a pair (g,h) might correspond several f, and Pythagoras fails.

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Behaviors of Fluid Inclusions in Dicumyl Peroxide single crystals versus temperature.

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Keywords: UV radiation, Impurities, Shrinking of Fluid Inclusions, Dicumyl Peroxide

Common behavior of fluid inclusions (FIs) during heating-cooling cycles of different crystals of organic compounds has shown a change in size and morphology from a rounded shape towards a faceted shape (i.e., 'negative crystal') when they are heated up. On cooling, they come back to their original rounded shape with a gas bubble inside which is not the most thermodynamically stable shape. Since different parameters affect the properties of fluid inclusions, it has been studied the effects of impurities on the formation of fluid inclusions and then its impact in the fluid inclusion behaviors. By contrast to this 'classical behavior', Dicumyl Peroxide (DCP) present some FIs that exhibit a rapid and drastic shrinking with a change in curvature upon fast cooling rates. In order to have a high density of FIs in crystals, the crystals were grown slowly by cooling an aqueous solution of ethanol with a large amount of CO_2. The FIs exhibiting shrinking on cooling often contains a large gas bubble. Depending on temperature, it takes from few minutes to several days to come back to rounded shape with a gas bubble. After a long period of time a more faceted shape reappears corresponding to thermodynamic equilibrium.

This new behavior is not true for all FIs in ethanol/DCP systems. Experiments of the effects of impurities through UV radiation on DCP crystals were made and compared with different cooling rates. Results indicate that crystals with more UV radiation show a more drastic shrinking at a higher temperature. Consistently, a larger chemical degradation of the crystals is correlated with more UV exposition. This degradation is initially visible at the surface of the crystals and subsequently in the inner state of the crystals. The time at which the curvature changes the most significantly is correlated with the nucleation of a gas bubble.

At slower cooling rates and in crystals without UV radiation the shrinking phenomenon is almost imperceptible in contrast with those irradiated with UV at slow cooling rates. The UV radiation is fostering the shrinking phenomenon but through optical microscope is visible that after more time crystals go to an irreversible change. The new reduced shape (shrunk) of FIs kept the same area as before. They went from a round shape to a concave shape with sharp corners and may be due to a transfer of matter foster by an excess number of impurities. The concave parts could be experimenting an inner crystallization and the sharp corners an outer dissolution.

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Mechanical behavior of carbon fibers reinforced PEEK laminates under fire conditions

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Keywords: Thermoplastic laminates, Kerosene flame, Mechanical testing, X-ray tomography

The current environmental concerns (CO2 emissions and energy demand) shows that one of the key issues in aeronautics is the design of lightweight structures [1]. Therefore, the integration of polymer matrix composites in structural parts is increasing [2]. However, due to their polymer matrix, their behavior is highly dependent on their thermal working conditions, which can be an issue in the case of an exposure to a flame. In fact, polymers decompose at high temperatures (400-600°C), which results in the formation of cavities filled with pyrolysis gas inside the plies. As the solid matrix is replaced by gas, there is less matrix available to ensure the load transfer. Thus, the mechanical behavior of the composite is altered [3]. For this reason, fire issue is of primary concern for aircraft manufacturers [4]. Understanding the thermomechanical behavior of composites under critical conditions (fire) is therefore essential. The literature on the fire behavior of composites has mainly focused on thermoset (TS) matrix composites [3] and much less on thermoplastic (TP) based composites [5,6].

To understand the relationship between the thermal aggression and the mechanical loading, it is important to dissociate the different phenomena that occur within laminates. This study focuses on a C/PEEK laminates with a QI stacking sequence. Several tests have been carried out. The thermal decomposition process in the first seconds of the fire exposure is first analysed in terms of porosity content; it correlates well with the evolution of the mechanical properties and thereby constitutes a good indicator of damage level. Then, the residual tensile properties at room temperature after exposure to the flame were determined. Finally, the in-situ tensile properties during the exposure was investigated to be compared to the residual behavior.

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Toward a benthic functional diversity approach of the English Channel coarse sediments

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Keywords: *Benthic macrofauna; Biodiversity; Functional diversity; Biological traits*

The English Channel is one of the most anthropized marine ecosystems in the world (e.g. [1]). It is exposed to both multiple anthropogenic activities (development of renewable marine energies, aggregate extraction, dredging and trawling) and natural disturbances (strong hydrodynamics, extreme events). These pressures occur in a context of climate change and modify the structure of benthic communities. One of the particularities of the English Channel is that it is composed of more than 80% coarse sediments.

Traditionally, these habitats have been mainly described using semi-quantitative tools and, more recently, studied from quantitative data to evaluate the functional response of these ecosystems to natural and anthropogenic disturbances. These data coupled with the analysis of biological traits of benthic macrofauna, will allow to better understand ecosystem functioning by linking abiotic parameters, community structure and traits distribution (e.g. [2]).

The two main objectives of this PhD thesis are: (1) acquire a better knowledge of coarse sediments of the Channel in a highly hydrodynamic environment; (2) couple traditional ecology studies (species diversity, abundances and biomasses) with functional diversity calculated from biological traits of species.

All the analyses will be based on the exploitation of different data sets describing the evolution of the diversity of coarse benthic communities exposed to various pressures.

Thus, this PhD thesis will provide a better understanding of the spatio-temporal organization of the functional diversity of the benthic macrofauna in the eastern English Channel. It will also provide a better understanding of the response of coarse sediment ecosystems to natural and anthropogenic disturbances.

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