

PRESENTATION OF PHD AND POST DOCTORAL RESEARCH WORK

2022-2023



REACTIONS AND CHEMICAL ENGINEERING
LABORATORY

UMR7274 CNRS—UL

NANCY



Présentation du livret et du laboratoire

Ce livret présente le travail des doctorants et des chercheurs post-doctorants du [LRGP](#) (Laboratoire Réactions et Génie des Procédés, UMR 7274 CNRS Université de Lorraine) pendant l'année universitaire 2022/2023.

Le LRGp est une unité mixte entre le [CNRS](#) et [l'Université de Lorraine](#), située à Nancy ([Région Grand Est](#), France), qui accueille jusqu'à 300 personnes, avec 15 chercheurs CNRS, 82 enseignants-chercheurs, 35 personnels administratifs et techniques permanents et environ 180 personnels non permanents (étudiants en master, doctorants, post-doctorants, chercheurs et personnels techniques sur contrats). Le laboratoire se trouve majoritairement sur le campus Granville, près de [l'ENSIC](#) (École Nationale Supérieure des Industries Chimiques), il est aussi implanté sur le Campus Brabois ingénierie, à [l'ENSAIA](#) (École Nationale Supérieure d'Agronomie et des Industries Agroalimentaires) et sur le campus de [l'IUT Nancy-Brabois](#). Il est donc fortement implanté sur la [métropole du Grand Nancy](#).

Le LRGp développe des connaissances scientifiques et technologiques pour la conception, l'étude, l'optimisation de procédés de transformation de la matière et de l'énergie, par voie chimique ou biologique. Ces thématiques comprennent les bases du génie des procédés, avec l'étude des transferts couplés de matière, de chaleur et de quantité de mouvement, ainsi que des fondamentaux de la chimie physique, de la cinétique, de la thermodynamique, et de la biologie. Le génie des procédés développe une méthode intégrative de l'ensemble de ces connaissances, avec des échelles spatiales allant de celle de la molécule jusqu'à celle du procédé industriel. Les recherches comportent le plus souvent une partie expérimentale et une partie modélisation, qui, de la même façon peut aller des approches très fondamentales de la physique et de la chimie moléculaire jusqu'à l'architecture des procédés

Les applications sont multiples et orientées vers les grands défis sociétaux actuels, comme la transition énergétique, la décarbonation de l'industrie, l'économie circulaire et le recyclage, les procédés pour l'environnement, les procédés propres, sûrs, intensifiés et durables, la production de médicaments par voie biologique et l'ingénierie des produits. Ces recherches ont pour dénominateur commun la prise en compte du procédé, de sa conception et de son optimisation. L'importance des aspects économiques et environnementaux est également bien prise en compte, car la plupart des recherches comporte une analyse du cycle de vie des procédés et une analyse économique.

Le LRGp évolue dans un écosystème particulièrement riche, au sein de l'université de Lorraine ([Pôle Scientifique EMPP](#)) et du CNRS ([INSIS](#)). Il bénéficie de la dynamique du dispositif LUE (Lorraine Université d'Excellence) et de la proximité avec les composantes de formation, de niveaux licences et master ; et de l'école doctorale [SIMPPE](#). Il entretient des partenariats académiques durables avec de nombreux laboratoires aux niveaux régional, national et international. Il a également une longue tradition de partenariats industriels, qui se traduisent par exemple, mais pas uniquement, par des laboratoires communs avec des groupes industriels comme EDF, Air Liquide et Avril. Le LRGp est aussi membre de [l'institut Carnot ICEEL](#) qui propose une approche maîtrisée de l'ingénierie permettant de créer de la valeur pour les industriels et les territoires.

Presentation of the booklet and the laboratory

This booklet presents the work of doctoral students and post-doctoral researchers at the [LRGP](#) "Reactions and Process Engineering Laboratory" (Laboratoire Réactions et Génie des Procédés, UMR 7274 CNRS Université de Lorraine) during the 2022/2023 academic year.

The LRGp is a joint research unit between the [CNRS](#) and the [University of Lorraine](#), located in Nancy ([Grand Est region](#), France). It employs up to 300 people, including 15 CNRS researchers, 82 professors and assistant professors, 35 permanent administrative and technical staff and around 180 non-permanent staff (master's students, doctoral students, post-doctoral students, researchers and technical staff on contract). The laboratory is located mainly on the Granville campus, near the [ENSIC](#) (École Nationale Supérieure des Industries Chimiques), but also on the Brabois engineering campus, at the [ENSAIA](#) (École Nationale Supérieure d'Agronomie et des Industries Agroalimentaires) and on the [IUT Nancy-Brabois](#) campus. It therefore has a strong presence in the "[Grand Nancy](#)" metropole.


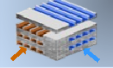



The LRGp develops scientific and technological knowledge for the design, study, and optimisation of processes for transforming matter and energy by chemical or biological means. These themes include the fundamentals of process engineering, with the study of coupled transfers of matter, heat and momentum, as well as the fundamentals of physical chemistry, kinetics, thermodynamics and biology. Process engineering develops an integrative method for all this knowledge, with spatial scales ranging from the molecule to the industrial process. Research usually includes both experimental and modelling aspects, which can range from very fundamental approaches to physics and molecular chemistry to process architecture.

There is a wide range of applications focused on today's major societal challenges, such as the energy transition, decarbonization of industry, the circular economy and recycling, processes for the environment, clean, safe, intensified and sustainable processes, the production of medicines by biological means, and product engineering. The common denominator of this research is that it takes into account the process, its design and its optimisation. The importance of economic and environmental aspects is also well considered, as most of the research includes an analysis of the life cycle of the processes and an economic analysis

The LRGp operates in a particularly rich ecosystem, within the University of Lorraine ([Pôle Scientifique/research department EMPP](#)) and the CNRS ([Institut INSIS](#)). It benefits from the dynamism of the LUE (Lorraine University of Excellence) scheme and its proximity to the training components, at bachelor's and master's levels, and to the [SIMPPE](#) doctoral school. It has long-standing academic partnerships with numerous laboratories at regional, national and international levels. It also has a long tradition of industrial partnerships, which include, but are not limited to, joint laboratories with industrial groups such as EDF, Air Liquide and Avril. The LRGp is also a member of [the Carnot institute ICEEL](#), which offers a controlled approach to engineering that creates value for industry and local communities

Le LRGP est organisé en cinq axes de recherche :

- PerSeVal : procédés pour l'environnement la sécurité et la valorisation des ressources
- PRIMO : procédé réacteur intensification membrane optimisation
- BioProMo : bioprocédés, biomolécules
- CiTherE : cinétique thermodynamique énergie
- Génie des produits : ingénierie pour les produits et les matériaux.

PROCÉDÉS POUR L'ENVIRONNEMENT, LA SÉCURITÉ ET LA VALORISATION DES RESSOURCES	<ul style="list-style-type: none"> • Économie circulaire • Hygiène industrielle • Dépollution • Procédés électrochimiques • Risques 	
PROCÉDÉS, RÉACTEURS, INTENSIFICATION, MEMBRANES, OPTIMISATION	<ul style="list-style-type: none"> • Réacteurs multifonctionnels • Procédés hybrides • Structure de procédés • Opérations intermittentes • Production décentralisée 	
BIOPROCÉDÉS - BIOMOLÉCULES	<ul style="list-style-type: none"> • Bioproduction cellulaire • Bioproduction microbienne • Procédés enzymatiques • Thérapie photodynamique • Ingénierie numérique 	
CINÉTIQUE - THERMODYNAMIQUE ÉNERGIE	<ul style="list-style-type: none"> • Cinétique radicalaire • Combustion • Conversion thermochimique • Thermodynamique • Fluides réactifs 	
GÉNIE DES PRODUITS	<ul style="list-style-type: none"> • Propriétés d'usage • Produits formulés complexes • Durabilité produit/procédé • Rhéologie • Modélisation 	

Il bénéficie de six services d'appui dédiés à l'administration, la logistique, la réalisation mécanique, l'électronique, l'informatique, et l'analyse chimique et biologique. Ces services permettent notamment de concevoir et de construire des dispositifs originaux pour les expérimentations à l'échelle pilote.

Dans ce livret, vous allez découvrir axe par axe les thématiques traitées par les jeunes chercheurs post-doctorant(e)s et doctorant(e)s, dans le cadre plus large des projets du laboratoire, et dans le respect de la confidentialité de certaines recherches. Je vous invite à prendre contact avec le laboratoire pour toute question et pour les sujets qui vous intéressent.

L'équipe de direction
vous souhaite une bonne lecture.
Bien cordialement,




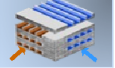



Isabelle Chevalot
Directrice Adjoint



Marie-Odile Simonnot
Directrice

The LRGP is organised into five research areas:

- PerSeVal: processes for the environment, safety and resource recovery
- PRIMO: membrane intensification reactor optimisation process
- BioProMo: bioprocesses, biomolecules
- CiTherE: kinetic thermodynamic energy
- Product engineering: engineering for products and materials.

PROCESSES FOR THE ENVIRONMENT, SAFETY AND RESOURCE DEVELOPMENT	<ul style="list-style-type: none"> • Circular economy • Industrial hygiene • Clearance • Electrochemical processes • Risks 	
PROCESSES, REACTORS, INTENSIFICATION, MEMBRANES, OPTIMISATION	<ul style="list-style-type: none"> • Multifunctional reactors • Hybrid processes • Process structure • Intermittent operations • Decentralised production 	
BIOPROCESSES - BIOMOLECULES	<ul style="list-style-type: none"> • Cell bioproduction • Microbial bioproduction • Enzymatic processes • Photodynamic therapy • Digital engineering 	
KINETICS - THERMODYNAMICS ENERGY	<ul style="list-style-type: none"> • Radical kinetics • Combustion • Thermochemical conversion • Thermodynamics • Reactive fluids 	
PRODUCT ENGINEERING	<ul style="list-style-type: none"> • Properties of use • Complex formulated products • Product/process sustainability • Rheology • Modelling 	

It has six support services dedicated to administration, logistics, mechanical engineering, electronics, IT and chemical and biological analysis. These services enable the design and construction of original devices for pilot-scale experiments.

In this booklet, you will discover the themes addressed by the young post-doctoral and doctoral researchers, within the broader framework of the laboratory's projects, and with respect for the confidentiality of certain research. I invite you to contact the laboratory if you have any questions or are interested in any of the topics.

The direction team
hopes you enjoy reading.
Best regards,



Pierre-Alexandre Glaude
Directeur Adjoint



Sandrine Jadelot-Nalet
Responsable Administrative

The Process Engineering and Reactions Laboratory (LRGP) is organised around 5 main thematic departments :

PErSeVAL: Processes for the Environment, Safety and the Recovery of Resources

PRIMO: Processes, Reactors, Intensification, Membranes, Optimisation

BioProMo: BioProcesses – BioMolecules

CITHERE: Kinetics, Thermodynamics, Energy

Product Engineering: Process Engineering for Products and Materials

***PErSeVAL* – Processes for the Environment, Safety and the Recovery of Resources**

Improving the quality of environments (air, water, soils), using resources wisely and controlling industrial risks have become fundamental stakes in a sustainable development and economy context. As an integrative science, process engineering can help in tackling these challenges. The themes of this strand therefore primarily concern reducing the negative impacts of industrial conversion processes on the system itself, its environment (natural environment, rural or urban areas) and people (exposure of operators and consumers to risks and pollution). The PErSeVal strand addresses these scientific challenges by developing processes that are inherently cleaner and safer, through multi-scale approaches in particular, and by designing innovative processes for effluent treatment (waste gas, aerosols and liquid) and pollution (e.g. soil contaminated by industrial activities). The products being treated generally derive their specific nature from their significant dilution (e.g. micropollutants), small size (ex. nanoparticles) or complex state (colloidal, chemical complexes, fractal state) in close interaction with their environment. The systems developed are often based on multiphase treatment processes which require a detailed study of the physical or reactional phenomena, combined with an environmental analysis of the processes (life-cycle analysis). Among these treatment or purification processes, particular attention is being devoted to those concerning adsorption phenomena, ion exchange and aerosol separation by filter media, granular bed filters and bubble columns. Building on the study of gas/solid particle flows, the PErSeVal strand also delves into hybrid mixture, mist and dust explosion phenomena. Lastly, with wise energy and resources management in mind, PErSeVal helps to promote the recovery of secondary resources that are currently not or only very little harnessed (hydrometallurgy for metal recovery, biogas plants, waste recovery, etc.) and to develop processes for using and generating renewable energy (electrochemical processes for energy conversion).

***PRIMO* – Processes, Reactors, Intensification, Membranes, Optimisation**

The research performed under this department is aimed at designing, studying and optimally carrying out new processes involving intensified reactors and microstructured systems, membrane technology, innovative gas-liquid contactors and supercritical processes. The study and development of multifunctional hybrid or coupled processes are thus considered fundamental in a bid to achieve technical and energy efficiency. Intensification, defined as all technologies and methods that enable yields to be increased, and the architecture of processes (Process Systems Engineering) , perceived as the spatial and temporal organisation of unit operations, form the building blocks of the department scientific approach of PRIMO.

The research combines experimental studies on pilots at different scales (intensified micro- and mini-reactors and microstructured systems, catalytic reactors, polymerisation reactors, gas-liquid and liquid-liquid contactors, membrane modules, supercritical extraction processes), specific parametric determinations and computational simulation studies often including computational fluid dynamics (reactive flows in mini-reactors, permanent or cyclic membrane gas separation processes, mass and heat transfer in clothes, evaporators). Beyond the simulation of processes, performed for its specific purpose and for confirming the experimental findings coming from different pilots, the validated models enable identification of processes' optimum working conditions and their control to be studied. Regarding optimisation and control, the research ties in with the general topic of process systems engineering (PSE), bearing both on methodologies (hybrid or global dynamic optimisation, nonlinear and predictive control, control of distributed parameter systems) and their applications (simulation of an adsorption process simulated under pressure via dynamic optimisation, control of reactors, exchangers).

BioProMo – Bioprocesses - Biomolecules

The activities of the BioProcesses-Biomolecules (BioProMo) department involve acquiring knowledge about, developing and controlling bioprocesses for producing diverse functional biomolecules. They are grounded in the development of a multidisciplinary, multi-scale approach: i)- the micro-scale at which enzyme activity or cell metabolism are characterised and measured (metabolic engineering, structural and functional quality of molecules produced, photodynamic therapy); ii)- the meso-scale at which we particularly assess the relations between the local, hydrodynamic and biochemical environment of animal cells and filamentous bacteria for quantifying macroscopic production kinetics; iii)- the macro-scale of the reactor and separator, whether membrane or chromatographic, at which the optimum working and performance conditions are determined by using computational approaches, such as multi-criteria optimisation, tailored to the specifics of bioprocesses. BioProMo scientific inquiries are primarily geared towards the societal challenges mainly concerning public health, the environment and sustainable development. To address these challenges, the topics explored fit squarely in with the application fields specific to (bio)process engineering, including white biotechnology (chemical inputs by fermentation, functionalised molecules, protein-driven biorefining), membrane processes (separation of complex mixtures of biomolecules), sensors (real-time monitoring of bioprocesses), genome engineering (biocatalysts, whether living or not, that must address the process's constraints), technology for medical imaging and cancer treatment (functionalised nanoparticles), production of molecules for therapeutic purposes (animal cell culture processes), cell and tissue engineering (stem cell expansion).

CiTherE – Kinetics, Thermodynamics, Energy

This department groups together the research activities associated with energy conversion processes, primarily thermochemical ones, and with products associated with or derived from such conversion processes. The research bears on the development of advanced kinetic and thermodynamic models, the development and control of such energy storage and conversion processes as heat pumps, combustion and pyrolysis reactions and biomass thermochemical conversion processes.

A significant part of the research focuses on developing detailed reaction mechanisms of the free-radical chemistry of combustion and pyrolysis, which are applied with a view to reducing greenhouse gas emissions and pollutants emitted by internal combustion engines, using conventional fuel (petroleum hydrocarbons) or new alternative fuels produced by biomass conversion. Through the consideration of complete reaction kinetics and the detailed thermodynamic description of phase transitions, significant progress is also possible in predicting the formation and exploitation of oil reservoirs. Significant attention is also devoted to thermodynamic studies for using neoteric solvents for extraction processes. The thermochemical recovery (combustion, gasification, pyrolysis, carbonisation) of lignocellulosic biomass for obtaining synthons (synthetic building blocks), 2nd generation biofuels or products, is also one of the department major themes and the "biorefinery" cross-cutting theme of the LRGP. Research encompasses the development of a systemic approach for analysing the different sectors with account taken of the various aspects associated with the environmental impact, via LCA type approaches and advanced multicriterion analysis. Energy recovery remains the very last stage once recovery of raw materials has been exhausted.

Product Engineering – Process Engineering for Products and Materials

Research conducted within this department has to do with product engineering, aimed at studying, designing and optimising the processes for developing multi-structured materials and products with several properties and functions of use. This work first requires an understanding of the links between the physical, physicochemical, biochemical, mechanical and structural properties at different scales of complex formulated products and materials, and then the translation of these properties into specific properties of use.

The end goal is to conduct the process in the best possible way to achieve control of the properties of use and performances sought-after for the products, as part of a wide diversity of innovative applications (safety, health, cosmetics, application products, catalysts ...). The processes developed and studied can be used to make a large number of products and materials. They include, for example reactive extrusion processes for polymer materials, crystallisation and precipitation processes for divided solids, or emulsification processes for emulsions. The formulated products and materials studied concern speciality applications: polymers, fibres, polymer matrix composites, granular media, nanoparticles and crystals, emulsions, suspensions, physical or chemical gels, etc. The multidisciplinary approaches developed within this department are grounded in the development of advanced tools and methods for characterising processes such as systemic rheology, in-line metrology and modelling and simulation to describe the multi-scale structuring of multi-constituent, typically multiphase and rheologically complex media, often entailing chemical reactions at the interfaces. The evolu-

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PERSEVAL

PROCESSES FOR ENVIRONNEMENT, SAFETY AND RESOURCE VALORIZATION

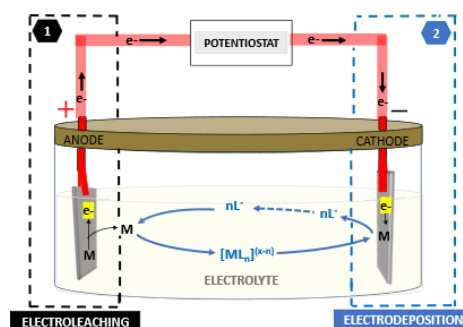
<p>2023</p> 	<p>Research subject: Selective recovery of precious metals from waste electrical and electronic equipment (WEEE) by electrochemical methods in ionic liquid</p> <p>Calogera Bertoloni (2nd year)</p> <p>Éric MEUX, François LAPICQUE, Sophie LEGEAI</p> <p>PERSEVAL, CEM (IJL)</p>	
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Keywords : Waste electronic and electrical equipments (WEE), precious metals, ionic liquids, deep eutectic solvents, electroleaching, electrodeposition

General context, scientific issues :

This thesis is part of the EE4Precious project, financed by ANR. The composition of precious metals in printed circuit boards waste is higher than that of primary resources. The recovery of these metals requires several steps with the use of powerful agents, that are harmful for the environment.

Illustration : New electrochemical process planned for the treatment of anodic sludge



Objectives and stakes :

This study consists of developing an electrochemical process for the recovery of silver, gold and palladium contained in an ultimate metallic fraction, provided by the industrial partner (TND) using process from electronic board waste. This process combines two steps in a single cell: anodic electroleaching of the sludge, and cathodic electrodeposition of the dissolved metal using deep eutectic solvents. The objective is to obtain, for both reactions, a maximum faradaic yield

Main results

Due to the strong complexing activity of these solvents, the EL step is efficient. The leaching runs carried out present gravimetric and ICP analysis yields close to 100%. According to EXAFS (Extended X-Ray Absorption Fine Structure) studies, silver is present as a mixture of $[\text{AgCl}_2]^-$ and $[\text{AgCl}_3]^{2-}$ in ET.2 Raman and UV-Vis spectroscopy analyses show that gold and palladium are in the leachate as $[\text{AuCl}_2]^-$ and $[\text{PdCl}_4]^{2-}$. Indeed, it has been shown that Au(I) dismutates slowly in the medium. Consequently, a study on the stability of the leachate is underway to work on this complex.



The cyclic voltammetry curves of the three metals shows that silver present in a metal mixture can be leached first (0,19 V/SHE), with a high selectivity. For deposition at the cathode, gold (0,65 V/SHE) is deposited first, then silver (0,09 V/SHE), and finally palladium (-0,22 V/SHE). These curve shows the electroleaching and electrodeposition reactions of the three metals occur within electrochemical window of deep eutectic solvent without undesired reactions from electrolyte.

Methodology :

Following the previous studies¹, the solvents used are ethaline 1:2 and propeline 1:3. There are a mixture of choline chloride (hydrogen bond acceptor) and ethylene or propylene glycol (hydrogen bond donor) with a molar ratio of 1:2 and 1:3 respectively. First, the experiments are carried out using pure metal phases, then alloys will be considered, and finally the polymetallic phase resulting from the processing of electronic cards, and a mini pilot will be designed

References :

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- [2] Abbott, A. et al, S. Phys. Chem. Chem. Phys. 2013, 15 (40), 17314–17323.
- [3] Villemejeanne, B., et al, E. J. Environ. Chem. Eng. 2022, 10 (3), 108004.

<p>2023</p> 	<p>Research subject: Influence of the geometric structure of filtration media on their performance</p> <p>Elise Cabaset (1st year)</p> <p>Dominique Thomas, Nathalie Monnier, Augustin Charvet</p> <p>PERSEVAL</p>	
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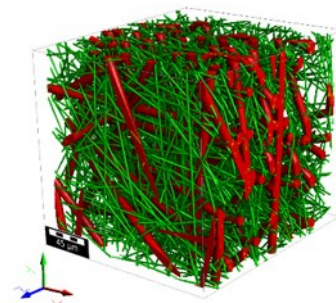
Keywords : permeability, filtration, fibrous media, aerosol, CFD, experiment

General context, scientific issues :

General context, scientific issues

Gas/particle separation processes are relevant in many fields, including environmental standards, operator protection, and air quality. Fibrous media are predominantly used for air filtration and purification.

Illustration : An example of microstructure generated by Geodict



Objectives and stakes :

A nonwoven filter medium is a complex structure consisting of random arrays of fibers that present a varying size distribution. The performance of a filter medium can be described by the pressure drop, which depends notably on the permeability according to Darcy's law at low Reynolds numbers. However, experimentally determining permeability is difficult due to numerous uncertainties, including the measurement of media thickness and the structure of the media, particularly its fiber size distribution. Various models have been proposed in the literature to determine the permeability of fibrous media, and no consensus has been reached.

Main results

A new correlation has been developed, inspired by the previous work of the team [1], which yields a difference between simulated and calculated results of less than 10% for our 66 simulations. Literature data also confirm the validity of this correlation. Additionally, simulations of structures composed of 3 and 4 diameters have shown small discrepancies.

An experimental protocol inspired by paper-making processes was established to create our own fibrous media. Fibers are suspended in an acidic solution and then filtered. The initial results seem promising for the creation of a homogeneous media. Experimental measurements of permeability are currently underway for different media composed of a single fiber diameter. Fibrous media composed of two types of fibers will be created and analysed subsequently.

After validating a correlation on permeability, a study will be conducted on aerosol filtration, in particular on single fiber efficiency by diffusion, interception, or inertia. These correlations will be extended to the case of bimodal or even multimodal fiber size distributions



Methodology :

One alternative to overcome these experimental biases is the use of numerical tools such as Geodict to build perfectly characterized 3D structures. 66 bimodal structures were created with different combinations of diameters, volume fractions, and packing density ranging from 1 to 20%.

A second way is to create one's own nonwoven filter medium using fibers, thereby ensuring a perfectly known fiber diameter distribution. Experimental techniques for characterizing fibrous media can also be improved

References :

[1] Thomas D. et al., Can J Chem. Eng. 2022;1-13

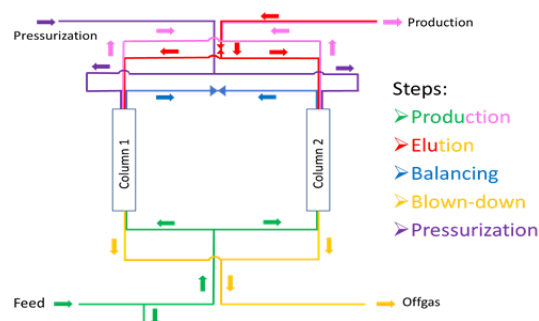
<p>2023</p> 	<p>Research subject: Impact of NO_x on CO₂ capture process: Pressure Swing Adsorption (PSA)</p> <p>Sayali Ramdas Chavan (Post-doctoral researcher)</p> <p>Cécile Vallières, Léa Sigot</p> <p>PERSEVAL, Air Liquide</p>	
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Keywords : Gas separation, pressure swing adsorption, CO₂ capture, process engineering

General context, scientific issues :

One of the popular industrial process for post combustion CO₂ capture is Pressure Swing Adsorption (PSA) due to its advantages [1]. Even though this technology is evolved [2], its operation in presence of impurities such as NO_x and SO_x remains unexplored.

Illustration : Simple representation of the two-column PSA cycle adopted for the study.



Objectives and stakes :

The following study is a joint project between LRGP and Air Liquide. The preliminary objective of this study is to characterise the experimental performance of different types of adsorbents for CO₂ capture in the presence of impurities (NO_x and SO_x). The project begins with the conceptualization of the lab-scale pilot followed by its design, construction, experimentation and optimization. Eventually, the work could be expanded to a predictive numerical model.

Main results

The pilot was first validated before starting the tests: proper functioning of instruments, leak detection, etc. Following, 8-steps PSA cycles were performed (illustration) to test the mass balance and pressure trends during individual steps. Currently, CO₂/N₂ adsorption PSA cycles have been performed and analysed for different CO₂ concentration and flowrates. The concentration trends of CO₂ during different steps and steady state are carefully studied. Some control experiments will be performed with binary gas mixture before introducing NO_x and O₂ in the process. Further, the tests will be carried out using different process parameters (pressure levels, residence time, gas concentrations etc.) and their effect on overall performance will also be studied. And the ultimate goal will be to test solid adsorbents provided by Air Liquide and identify underlying CO₂ adsorption mechanisms in PSA (in presence of NO_x and O₂). Lastly, since the project is confidential, the technical details, materials, results and detailed process scheme could not be disclosed.

Methodology :

First part of the project was dedicated to the sizing [3] and conceptualization of the process. The piping and instrumentation diagram was also drafted during this period. Consequently, the instruments have been ordered and parallelly a 3D visualization model, an electrical scheme and electronic circuits were completed. Eventually, the lab-scale pilot was set-up and ready in the first year.

This semi-automated test bench is being used to perform PSA cycles. The minimum requirement is a basic four-stage Skarstrom-type cycle (pressurization, adsorption, blowdown and purge/desorption) with an additional balancing step to save energy. The process is equipped with 2 columns to ensure quasi-continuous gas separation. The dynamic process parameters such as pressure, temperature, flowrate, and gas concentration are monitored in real time with the help of sensors, flow meters and gas analysers. The feed gas is mixed synthetically using the mass flow controllers to simulate post-combustion flue gases.

Notably, the pilot will be operated (hands-free) inside a ventilated cabin as a safety measure

References :

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- [3] G. de SOUZA, 'Purification des gaz par le procédé PSA', *Techniques de l'Ingénieur*. <https://www.techniques-ingenieur.fr/base-documentaire/procedes-chimie-bio-agro-th2/operations-unitaires-traitement-des-gaz-42485210/purification-des-gaz-par-le-procede-psa-j3606/> (accessed Jun. 29, 2022)



Keywords : lattice Boltzmann, viscoelasticity, coalescence, droplet, multiphase flow, Oldroyd-B

General context, scientific issues :

Droplet wetting and spreading on a liquid or solid surface is a major field of interest in both academic and industrial domain. The impact velocity as major parameter in this usually fast phenomenon, the droplet may splash, bounce, or coalesce according to the nature of the surface. In the recent years several experiments on the initial moment of the coalescence have been performed [1], but we still do not fully understand the physical mechanisms involved. Some numerical experiments have been made over the past years on splashing, some of them have been made with axisymmetric geometry [2]. The coupling with a viscosity model is a new challenging area. Most of the coupling using a 2D model with an Oldroyd-B model [3], the coupling with the Maxwell model have been made with monophasic model

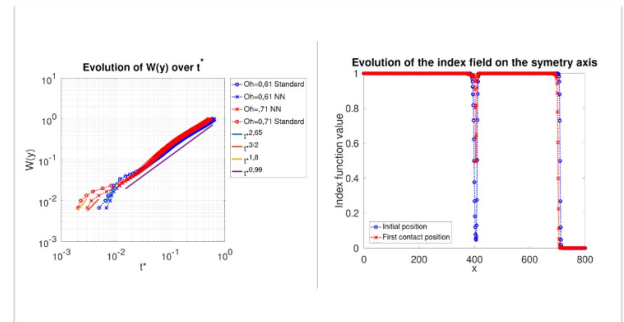
Objectives and stakes :

The main objective is to compute by the Lattice Boltzmann method (LBM) an axisymmetric diffuse interface multiphase with high density ratio regarding a stable numeric approximation of the complex phenomenon. We also have to add an Oldroyd-B model for the elasticity. The model is validated by comparing the experimental results and the numerical ones for the evolution of the liquid bridge between the droplet and liquid surface that is created during the coalescence.

Methodology :

To compare the results issued from the experiments we develop two different numerical experiments. In a first step we will only use the LBM in order to not have the viscosity model and compared with the Newtonian case. In a second step we will add the viscosity model to compare with the other case. The dimensionless number that is relevant is the Ohnesorge number $Oh = \eta_1 / \sqrt{\rho_1 D \sigma}$, the only parameter that we can change to change the value of is the surface tension parameter. The numerical strategy is adopted as follows: firstly, we initialize the computational field. Then we determine the viscosity part with the Oldroyd-B model, after the LBM is computed by coupling with the external force of the Oldroyd-B model. Then the boundary conditions are applied to the model. At the end the main fields with ρ the density, the velocity field and the pressure field are numerically obtained

Illustration : Evolution of the liquid bridge between the droplet and the flat liquid surface over the dimensionless time



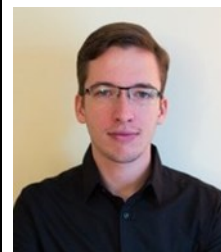
Main results

We have developed an axisymmetric high density ratio lattice Boltzmann method coupled with the Oldroyd-B model. In order to validate the LBM, we compare our numerical results with the experiment ones for a droplet spreading on a liquid surface. We found the similar law and there is nearly no difference between fluids of different viscoelasticity including Newtonian fluids. Most of the difference took place at the beginning of the coalescence, probably due to the numerical imprecision at this stage. Also, we found a power law with an exponent superior at 1 at the beginning. We tested the Maxwell model and found the similar results for the evolution of the liquid bridge with a power law of an exponent of 1.

Further investigation is performing to better understand the ultra-fast coalescence through the evolution the liquid bridge at its very initial stage, a domain that experiments could not accede easily

References :

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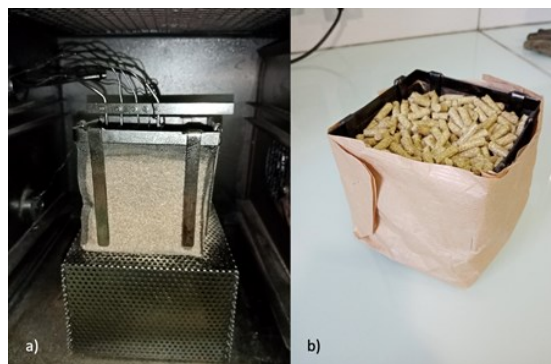


Keywords : self-heating, diffusion, biomass piles

General context, scientific issues :

Biomass is increasingly used as an energy source, but it can undergo self-heating accidents [1]. The shape and size of biomass piles can affect their self-heating behavior. However, predicting the impact of porosity and permeability on thermal stability is complex

Illustration : : a) Instance of basket test with fine powder, b) wire-basket filled with pellets and wrapped with paper



Objectives and stakes :

This study investigates the interplay between particle size, oxygen accessibility, and thermal stability of biomass piles. Various parameters were varied: basket size, particle size distribution, and storage wrapping. A design of experiments was employed and a model incorporating mass and heat transfer was developed to represent thermal behavior.

Main results

TGA showed water loss up to 100 °C, hemicellulose reaction below 250 °C, and cellulose and lignin reactions above 320 °C. Activation energies for hemicellulose and cellulose/lignin combustion reactions were determined using the Flynn-Ozawa-Wall method: 50.6 and 45.2 kJ/mol, respectively. The thermal stability tests using basket ovens showed repeatability. Temperature evolution within the basket showed non-symmetrical propagation of thermal waves and the importance of internal convection. Combustion gas analysis indicated a CO/CO₂ ratio increase after the crossing point, demonstrating the potential for early detection of self-heating. The influence of biomass size, temperature, and basket size on thermal stability was investigated using factorial and Doehlert designs, showing non-linear behavior and the impact of bed permeability and oxygen accessibility. Bagging the basket increased thermal stability, particularly at lower temperatures.

A 3D-model for biomass piles in a quarter basket was developed using finite volume method, validating heat transfer within the piles.

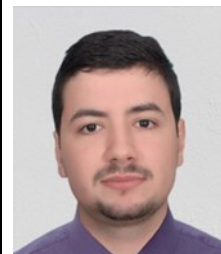
Methodology :

Miscanthus was used in various forms from raw pellets to fine powder. Thermal stability was evaluated using basket tests and thermocouples following ISO/TS 20049-2 standard [2]. Ignition criteria and self-heating behavior were analyzed using Frank-Kamenetskii theory. Flue gases were collected and analyzed using μ GC.

Thermogravimetric analyses (TGA) were conducted under air on biomass samples using various constant temperature ramps to determine combustion kinetics and activation energy using integral (FWO) and differential methods (Friedman and Kissinger).

References :

- [1] Restuccia F., Fernandez-Anez N., Rein G., 2019, Experimental measurement of particle size effects on the self-heating ignition of biomass piles: Homogeneous samples of dust and pellets, *Fuel*, 256, 115838.
- [2] ISO/TS 20049-2, 2020, Solid biofuels - Determination of self-heating of pelletized biofuels - Part 2: Basket heating tests, International Organization for Standardization



Keywords : CO₂ conversion, wastewater treatment, electrochemical advanced oxidation process

General context, scientific issues :

The scarcity of water is a worldwide growing concern, and the reuse of treated wastewater is playing a crucial role in managing water resource. Moreover, the release of CO₂ in the atmosphere from treatment plants can be an environmental concern

Objectives and stakes :

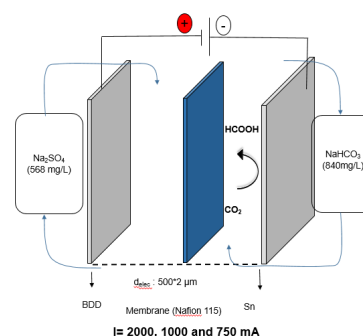
The reuse of treated wastewater is an emerging solution to the water crisis. The objective of this thesis is to valorize the CO₂ generated during the mineralization of organic pollutants in wastewater by converting it into added-value organic compounds such as formic acid. In addition, the CO₂ can come from the (bi)-carbonates present in wastewater. The challenge remains in performing such processes at ambient temperature and pressure with the highest conversion yield and without the external addition of chemicals.

Methodology :

An electrochemical divided cell consisting of two parallel plates placed vertically was used (Figure 1). The anode consisted of boron-doped diamond (BDD) deposited on niobium with a geometric area of 50 cm², while tin was used as the cathode with an area of 50 cm². Our research specifically focuses on studying the influence of the main operating parameters such as current density, inter-electrode distance, pH and electrode materials. The degree of solution complexity will be progressively increased from synthetic to real effluents, to better understand the mechanisms involved.

For all experiments, a 500 mL synthetic effluent was prepared containing a concentration of 0.84 g/L sodium bicarbonate (NaHCO₃). Since the solution pH is varying during the electrochemical treatment, the influence of pH on the carbonates conversion into CO₂ and then into formic acid has been particularly investigated with our setup at various controlled pH (2-8). The electrochemical cell was operated in closed recirculated mode with the help of a peristaltic pump (Masterflex, Cole Parmer). Electrolysis was performed using a power supply (HAMEG, Rohde & Schwarz) to control the applied current density.

Illustration : Experimental setup



Main results

The evolutions of formic acid concentration and of total organic carbon (TOC) content as a function of electrolysis time and solution pH are displayed in Figure 2.

The highest yield of formic acid formation was observed at a pH of 4, with a concentration of approximately 45 mg/L. Increasing the pH from 4 to 6 and 8 makes decrease the production of formic acid, reaching 41 mg/L and 20 mg/L respectively. Similarly, the evolution of the TOC concentration followed the same trend as the formation of formic acid. Therefore, a solution pH of 4 was optimal to favor formic acid generation, which was in agreement with literature using an alternative setup.

According to literature, less formic acid generation at higher pH may be attributed to a decrease in proton concentration, which plays a key role as a source of hydrogen in the conversion of CO₂ to HCOOH. In contrast, a decrease in bulk pH from 4 to 3 resulted in a slight decrease in the final formic acid concentration. This may be attributed to the greater impact of hydrogen evolution under these conditions. A further step will be to better control the kinetics in order to reach the optimal pH without external acidification of solution.

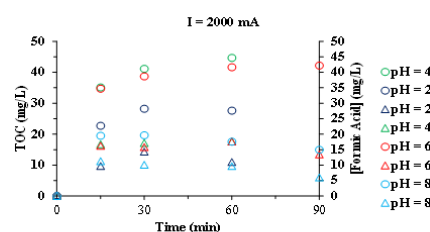




Figure 2: Evolutions of formic acid concentration (○) and of TOC (Δ) as a function of electrolysis time and solution pH.

<p>2023</p> 	<p>Research subject: Modeling, simulation, and experimentation of the digestion tank in a phosphoric acid manufacturing process</p> <p>Sanae EL MISAOU (5th year)</p> <p>Abderrazak LATIFI, Mohamed SALOUHI</p> <p>PERSEVAL, OCP, UM6P</p>	
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Keywords : phosphoric acid manufacturing process, phosphate rock dissolution, digestion tank, modeling, simulation, optimization, experimentation

General context, scientific issues :

Phosphoric acid is used in a variety of industrial processes, including the production of fertilizers, food, and even pharmaceuticals. Its manufacturing process is one of the most important in the phosphate industry [1]. Due to a lack of thermodynamic, kinetic, and hydrodynamic data, as well as a lack of knowledge on the many complex phenomena involved in the process, the design and operation of these processes continue to pose several challenges. It is therefore critical to understand these phenomena in order to accurately model and optimize process performance in general, and the digestion tank in particular, which is the heart of the process.

Objectives and stakes :

This research aims to determine the operating conditions that maximize the yield and purity of the phosphoric acid produced in the existing processes and to design new compact, intensified, efficient, and sustainable processes. The ultimate objective is to increase the value of phosphoric acid by extending its area of applications and utilizing it in the synthesis of highly valuable products.

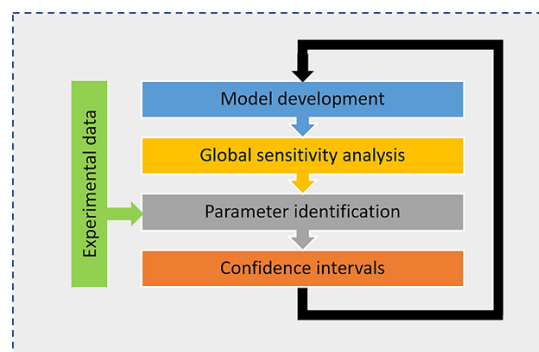
Methodology :

The approach adopted consists in the development of precise first-principles models with strong and permanent interactions with experimental measurements. The optimal process design and operation will then be achieved using the validated models. The phenomena occurring in the digestion tank are more specifically covered in this work, including the dissolution of phosphate ore in phosphoric acid and the crystallization of gypsum in the presence of a sulfuric acid solution.

Phosphate dissolution is regarded as a non-catalytic liquid-solid reaction (i.e. shrinking core model) with product elimination [2]. Furthermore, in order to better understand the kinetics of the dissolution mechanism, including the determination of the limiting step, an experimental approach is elaborated [3]. In addition, by taking nucleation and growth phenomena into account, a crystallization model was developed.

By coupling the dissolution and crystallization models, a global model is obtained. It enables the majority of the complex phenomena present in the digestion tank to be satisfactorily described.

Illustration : Diagram of the first-principles modeling approach

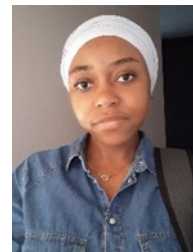


Main results

The models are implemented and solved within gProms software. The model predictions deal with the concentration profiles in the liquid film surrounding the phosphate particles and in the liquid mass inside the digestion tank, the conversion rate by the dissolution step, the nucleation rate, the growth rate, the supersaturation rate, and the crystal size distributions by the crystallization step [4]. To determine the unknown model parameters from the available measurements, statistical techniques, reconciliation of static and dynamic data, optimal experimental design, and global estimability analysis are developed (Illustration). The model outputs are compared to the experimental results. Once the model is validated, it will be used to identify optimal operating conditions that will improve the efficiency of current phosphoric acid manufacturing processes.

References :

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Keywords : LOCA (Loss Of Coolant Accident), clogging, SA (Severe Accident), filter, chemical effects

General context, scientific issues :

The LOCA is caused by a breach in the primary circuit of a nuclear reactor. The emergency systems RIS/EAS are set off to ensure reactor cooling and reduce containment pressure. These systems switched to recirculation mode to reintroduce the water collected in the sumps located at the bottoms of containment when the level tank initially used is low [1]. Debris are generated and can be transported through the sump filters contributing to physical and chemical clogging of the filters. Chemical contribution corresponds to precipitates/gels of "chemical effects" which are present in solution. This clogging can hamper the operation of the RIS/EAS recirculation systems by limiting the circulation of water and potentially leading to a SA due to a lack of cooling of the reactor core. SA corresponds to the degradation of reactor fuel by complete meltdown of the core [2].

Objectives and stakes :

The objective of this research is to study the nature of these chemical effects, the parameters conditioning their reactivity (formation of precipitates/gels) and their extent beyond which the risk of clogging is proven in the event of LOCA and SA. Characterization of solution, chemical speciation and precipitation have been performed by ICP-EAS, MEB-EDX, DRX and IFTR-ATR.

Methodology :

The methodology developed by Coralie Le Maout Alvarez [3] on 900 Mwe PWRs in LOCA situation will be applied during this PHD-thesis work. Three directions of work are studied: first part is dedicated to static tests to define the parameters (temperature and concentration) favorable to the formation of precipitates based on mineral species released in solution from the dissolution of the debris. Afterward, the thermodynamic approach is studied thanks to geochemical calculation tools (CHESS and PREEQC) which enables possible to couple the experimental data and simulations. This will ensure the consistency between the precipitates obtained and those predicted and to facilitate the interpretation of the experimental results. Finally, the dynamic conditions tests will be performed in the recirculation loop to identify the extent of the chemical effects on the pressure drop of the filters.

References :

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- [3] C. Le Maout, « Etude expérimentale des effets chimiques sur le colmatage des filtres dans l'industrie nucléaire », Thèse de doctorat, Université de Lorraine, 2019.

Illustration : Scheme and photographs of the experimental set-up for static tests (COPINES)

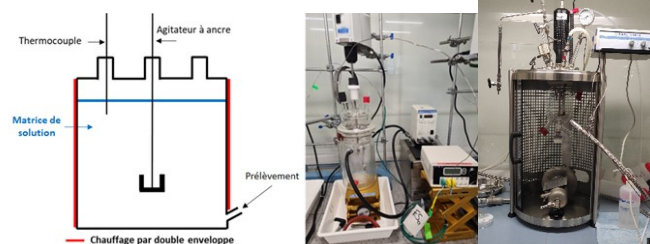
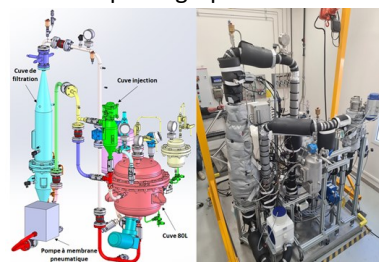




Figure 2: Scheme and photographs of the COPIN filter loop



Main results

Dissolution tests of debris likely to be generated in case of LOCA for EPR and PWRs were carried out. The objective was to determine the dissolution kinetics of the main elements of the debris. The tests were carried out in a matrix of boric acid and sodium hydroxide solution according to the reactor type conditions (PWR or EPR) at various temperatures and pH. The dissolution of 1g fiber 785 NE containing 65% silicon (SiO₂) et 30% calcium (CaO) in H₃BO₃/NaOH at pH 8, showed that Ca dissolves more compared to Si with a percentage of Si at 13%mass and Ca at 11.5%mass which dissolves at 80°C for 52h. Different tests was carried out with 1g fiber NUMINE containing 52% SiO₂ and 43% CaO at pH 7 and 8 with variation of temperatures at 60°C and 80°C. The results show that the dissolution of Si and Ca depends on the temperature and the pH however in terms of dissolved species, Si dissolves more compared to Ca regardless of the conditions. For example, 21.60%mass of Si dissolved at pH 7 during 74h at 80°C contrariwise 2.26%mass of Ca dissolved in the same conditions. The concrete used in ERP containing 65,56% SiO₂, 13,44% CaO and 4,6% Al₂O₃ was studied for 60°C and 80°C at pH 7. The results showed that the dissolution depend on the particle size of concrete. However, Ca dissolved more than Si never mind the porosities or temperature.

<p>2023</p> 	<p>Research subject: Metal recovery by agromining in French Guiana</p> <p>Thomas MONOT (2nd year)</p> <p>Baptiste LAUBIE, Marie-Odile SIMONNOT</p> <p>PERSEVAL SOLEO</p>	
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Keywords : Agromining; Aluminium; Hydrometallurgy; French Guiana;

General context, scientific issues :

An aluminium hyperaccumulator has been identified during a prospection campaign in French Guiana. Its discovery makes the development of aluminium agromining in this region a viable option.

The aim of this thesis is therefore to develop a process aimed at extracting and valorising aluminium from this hyperaccumulator

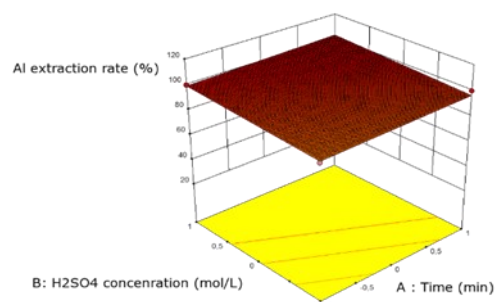
Objectives and stakes :

The first objective of this work is to develop a protocol to maximize aluminium extraction from the ash. To achieve this, multiple choices must be made, including the matrix used, the combustion temperature of the biomass, the chemicals used for the digestion step, and the extraction conditions. Then, an optimization step will be carried out to optimize the process of aluminium extraction, and increase the purity of the final product.

Methodology :

Hyperaccumulator biomass and ash incinerated at different temperatures were first characterized by several analytical techniques. Elemental analysis showed that ash was contained mainly aluminium, calcium, magnesium and potassium. The choice was made to use ash incinerated at 900°C as the matrix, because of their high concentration in aluminium. As ICP-OES analysis revealed a low concentration in silicon (1.5% w/w), the acid process path was chosen to extract the aluminium. 1 Sulfuric acid was chosen as it is recognized in the literature as an efficient chemical for aluminium extraction. 2 In addition, sulfuric acid allows for the synthesis of aluminium sulphate and potassium alum, products with large ranges of application. A factorial design of experiment with 3 factors (temperature, time and sulfuric acid concentration) was used to determine the extraction conditions, with the aim to reach a 100% extraction rate. The CHESS software was then used to develop a protocol aiming at precipitating calcium in the form of gypsum by increasing pH through addition of lime, which was subsequently filtered out of the solution. Aluminium sulphate crystallization was finally carried out by low pressure evaporation.

Illustration : Aluminium extraction rate (%) at 90°C function of H₂SO₄ concentration and leaching duration.





Main results

Design of experiment showed that temperature was the most important parameter to achieve high aluminium extraction rate. A 100% extraction rate was achieved even with low concentration sulfuric acid at 90°C. The pH of the leachate was successfully increased by addition of lime milk to the target range, however elemental analysis of the final product revealed it still contained high amounts of calcium. The precipitation step appeared to have no effect on the calcium concentration of the final product, but further experiments are needed to confirm these results. In addition, elemental analysis of the lime added to increase the pH revealed that a fraction of the aluminium was trapped in the lime milk and lost during the filtration step.

References :

1. Ding J, Ma S, Shen S, Xie Z, Zheng S, Zhang Y. Research and industrialization progress of recovering alumina from fly ash: A concise review. Waste Management. 1 févr 2017;60:375-87.
2. Wei C, Cheng S, Zhu F, Tan X, Li W, Zhang P, et al. Digesting high-aluminum coal fly ash with concentrated sulfuric acid at high temperatures. Hydrometallurgy. 1 sept 2018;180:41-8

<p>2023</p> 	<p>Research subject: Membrane process development to minimize environmental impacts of nickel recovery by agromining</p> <p>Thomas Porqueddu (2st year)</p> <p>Baptiste Laubie/Marie-Odile Simonnot</p> <p>PERSEVAL</p>	
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Keywords : hydrometallurgy, membrane processes, separation, nickel, ion transport modelling, speciation

General context, scientific issues :

This work falls within the context of the agromining chain, which aims to recover metals extracted from soils using plants. The objective of this work is to recycle the acid contained in hyperaccumulator plant ash leachates using membrane processes. Membrane technology was chosen because it is known to reduce the environmental impact of industrial processes, especially if they involve many chemicals. It also offers high selectivity in the separation of metals, but the choice of best operating conditions depends very much on the speciation of the leachate.

Until recently, membranes could not be used often in this kind of project, because of chemical and physical limits. Today, there are membranes capable of withstanding the difficult conditions of industrial leachates, at very low pH.

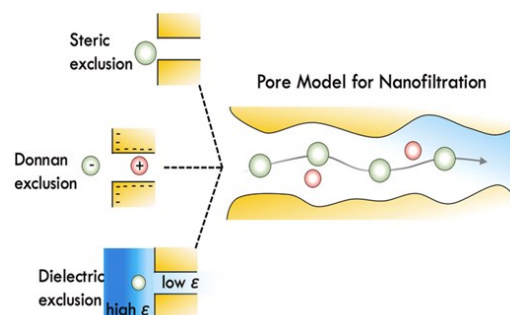
Objectives and stakes :

The objective is to experimentally study the membrane separation of dissolved metals in a highly acidic solution and to build a mathematical model to understand the different phenomenon behind the separation.

Methodology :

The filtration operation consists of effectively separating the metals in a concentrated stream, so that a metal-poor, proton-rich stream can be recovered for further leaching. Nanofiltration is carried out at a pressure of between 5 and 15 bar. The leachate is then diluted by 2, 4, 8, 10 and 20 times to study the influence of the leachate ionic strength on the rejection rate of divalent metals. Speciation of each leachate is performed using PHREEQC software and the SIT and PHREEQC databases. This step is necessary to proceed to the modelling of ion transfer through the nanofiltration membrane using the SEDE (Steric, Electric and Dielectric Exclusion) model. This model allows us to simulate the separations by considering steric hindrance, the Donnan effect and the effects linked to the differences in dielectric constants between the solution outside and inside the membrane (Born effect and mirror effect). This gives us a better understanding of which effect is predominant in the separation depending on the ionic strength of the feed solution.

Illustration : Diagram of the SEDE model [2]



Main results


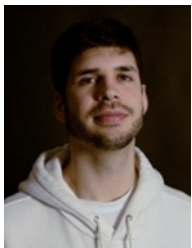
According to the literature, the higher the applied pressure, the greater the flow rate of liquid through the membrane, and the greater the rejection rate. The experiments were operated at 15 bars to determine the maximum rejection rate at a given ionic strength. The results obtained allow us to conclude that there is an optimum ionic strength for nanofiltration with agromine leachate: the ionic strength of 0.36 mol/kgw is the one with the highest rejection rate for divalent elements (85%). For undiluted leachate, this rejection rate is 35%, which is abnormally low.

This result could be explained by the model, which is in agreement with the observation. Indeed, it could be shown that at high ionic strengths (> 0.72 mol/kg) the Donnan effect is preponderant, whereas at lower ionic strengths, the steric exclusion dominates the matter transfer. The latter is directly correlated to the variation of the mean pore radius of the membrane, which increases with ionic strength, as experimentally proven. The effects related to the differences in dielectric constant do not play a significant role in the separation of the solutions studied in this context.


This work will now make it possible to estimate the proton saved, as a function of the operating conditions.

References :

1. Y. Lanteri et al Evaluation of the steric, electric, and dielectric exclusion model on the basis of salt rejection rate and membrane potential measurements, *Journal of Colloid and Interface Science* 331 (2009) 148-155
2. Ruoyu W. et al, 2021. Pore model for nanofiltration: History, theoretical framework, key predictions, limitations and prospects, *Journal of Membrane Science* vol 620:118809



<p>2023</p> 	<p>Research subject: Metrology and methodology for analyzing risks related to exposure to natural stone dust.</p> <p>Adrien Rizza (1st year)</p> <p>Dominique Thomas, Olivier Dufaud</p> <p>PERSEVAL</p>	
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<p>Keywords : Dust stone, exposure measurements, security, aerosol metrology</p>

<p>General context, scientific issues :</p> <p>Stone industry professionals are exposed to various dust particles. A recent decree has set new limits for total dust and respirable dust exposure. This raises questions about metrology and process compliance to protect workers.</p>	<p>Illustration : Operator's exposure to siliceous dust during a sandstone cutting operation.</p> 
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<p>Objectives and stakes :</p> <p>The concentration, particle size distribution and chemical composition (especially silica content [1]) of the aerosols generated are important parameters for risk assessment. The objectives are to develop innovative metrology to better assess the occupational exposure of employees and promote risk management at each stage of natural stone preparation.</p>	<p>Ongoing activities and perspectives</p> <p>A census of current regulations in France and Europe has been conducted to list their requirements and developments, and to better define the objectives of the measurements. Visits to workshops and quarries have provided an overview of natural stone shaping processes and have also allowed the assessment of workers' exposure to this type of dust.</p> <p>To address the research problem, two types of measurements will be implemented:</p> <ul style="list-style-type: none"> - Ambient measurements, to determine dust concentrations in the workshop, analyze particle size, and measure ambient parameters such as humidity and air velocity, which can influence particle movement. - Measurements on workers, to determine the nature of inhaled particles and classify their particle size distribution. These measurements will be conducted according to pre-defined procedures. <p>Thanks to these experimental results and additional research work, it will be possible to recommend appropriate solutions (ventilation, capture, enclosure, wet work, etc.) to comply with occupational exposure limits by reducing concentrations. These solutions can be subjected to CFD-type simulations to assess their effectiveness.</p>
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<p>Methodology :</p> <p>The methodology adopted to address the issue is as follows:</p> <ul style="list-style-type: none"> • Proposing and developing metrology solutions suitable for natural stone dust and the variability of implemented processes. • Considering the aerodynamics of relevant premises to establish relationships between ambient measurements (fixed point) and exposure measurements (on workers). • Creating a comprehensive methodological guide for risk assessment and control for employees in this professional sector, to comply with regulations, using exposure measurement methods and tools adapted to the diversity of the occupations involved. 	<p>References :</p> <p>[1] Rokni, M., Mohammadyan, M., Hashemi, S.T., Asadi, S.M., Boogaard, P.J., Heibati, B., Yetilmezsoy, K., Abdul-Wahab, S.A. Risk assessment of workers exposed to crystalline silica aerosols (2016) Human and Ecological Risk Assessment, 22 (8), pp. 1678-1686.</p> <p>Gautam, S., Prusty, B.K., Patra, A.K. Dispersion of respirable particles from the workplace in opencast iron ore mines (2015) Environmental Technology and Innovation, 4, pp. 137-149.</p>
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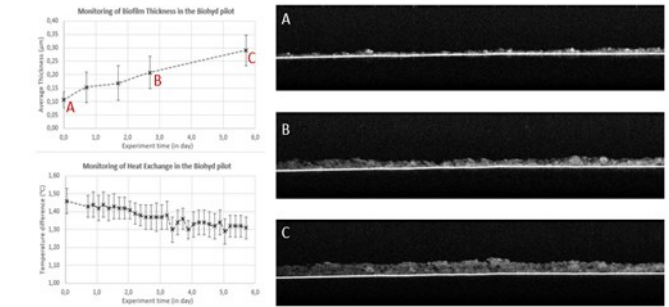
<p>2023</p> 	<p>Research subject: Project HyBioT : Biofouling impact on heat transfert in cooling systems</p> <p>Kevin Roudaut (research engineer)</p> <p>Nouceiba Adouani, Eric Olmos</p> <p>PERSEVAL, EDF</p>	
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Keywords : Heat exchangers, Biofilms, Biofouling, Experimental pilot, Hydrodynamics, Modeling

General context, scientific issues :

In France, power plants use natural water (i.e. rivers) in their cooling system to evacuate heat excess. However, those conditions enhance fouling and biofouling on heat exchangers surfaces. These accumulations of matter, especially biofilms, reduce significantly the efficiency of heat transfer. Furthermore, biofouling can cause corrosion and biological pollution to receiving aquatic environments.

Illustration : Evolution of heat exchange in relation to biofilm thickness during an experiment.



Objectives and stakes :

- With a laboratory pilot, identify experimental conditions that result in the lowest biofouling.
- Design a mathematical model coupling hydrodynamics, biofouling development (including the kinetics of growth, death and detachment), heat and mass transports.
- Determine the impact of those phenomenon and their inter-connection.

Main results

Depending on the experiment conditions (heat temperature, water temperature and flow), different biofilms structures should appear, regardless of the frequency of nutrient addition. Indeed, in higher shear stress, biofilm detachment would happen more often reducing its average thickness. Temperatures that are more suitable to microbial growth should result in a better biofouling. Microbiological composition of the biofilm should also depend from this parameter. The properties of the biofilm (thickness, area of covering) should impact the heat exchange, reducing it significantly if enough biofouling is happening in the pilot.

Several experiments of several weeks were performed to start collecting data that could be used to create a mathematical model. This model should be able to optimize the cooling process, predicting biofilm development and thermal efficiency loss and adapting the settings (flow rates, shear stress, temperature) to reduce this impact. It could also be used to determine the threshold of interference of biofouling to reduce biocides use.



Methodology :

A laboratory pilot reproducing large operative conditions of actual industrial heat exchangers used in power plants is used to perform an experimental design. Natural water collected from different rivers, heated at different temperatures, flows under several hydrodynamic conditions (fluid velocity, turbulence regime, shear stressing) and to accelerate biofouling, nutrients are added regularly.

Temperature sensors will allow heat exchange calculations. The incoming and outgoing water from the pilot will be chemically and biologically characterized. The structures and microbiological composition of biofilms will be analyzed with microscopic (Optical Coherence Tomography) and metagenomics techniques.

References :

- [1] N. Jourdan, « Hydrodynamique dans les circuits de refroidissement industriels : influence sur les phénomènes d'encrassement, caractérisation et modélisation », Thesis, Université de Lorraine, 2020.
- [2] H.-C. Flemming, « Microbial Biofouling: Unsolved Problems, Insufficient Approaches, and Possible Solutions », in Biofilm Highlights, H.-C. Flemming, J. Wingender, et U. Szewzyk, Éd. Berlin, Heidelberg: Springer, 2011, p. 81 109.
- [3] Z. Xu, J. Wang, L. Xia, et Y. Zhang, « A biofouling thermal resistance model with a growth term of surface biofilm on heat transfer surface », International Journal of Thermal Sciences, vol. 161, p. 106699, mars 2021.

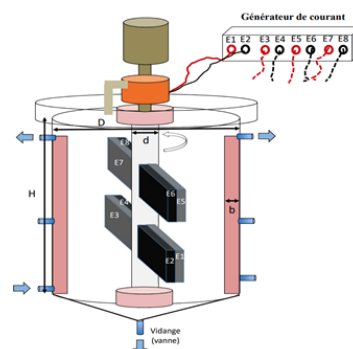
<p>2023</p> 	<p>Research subject: Development of a hybrid and innovative electrochemical process for the treatment and/or recycling of industrial and/or urban wastewater</p> <p>Aurélien Ruffet (Engineer) Emmanuel Mousset PERSEVAL, Tree Water</p>	
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Keywords : Electrolysis, Reactive electro-mixing, Thin film cells, Wastewater treatment

General context, scientific issues :

The growing demand for water in the various economic sectors leads to the production of increasingly complex water effluent used along with the rise of bio-recalcitrant compounds release [1]. Wastewater treatment plants (WWTPs) are finding it increasingly difficult to eliminate these types of compounds [2]. Therefore, the use of advanced physico-chemical technology such as emerging electrochemical process seems necessary.

Illustration : Schematic diagram of a reactive electro-mixing reactor.



Objectives and stakes :

The main objective of this project is the development of an emerging technology involving rotating electrochemical cells, called electro-blades, that should be able to intensify mass transfers, while increasing treatment capacities and limiting clogging phenomena with real effluents.

Main results

The studies have shown that with a rotation speed of 15 rpm, it is possible to achieve a significant elimination of phosphates (82%), which is up to 1.61 times better than that of the thin film reactor, with a similar energy consumption.


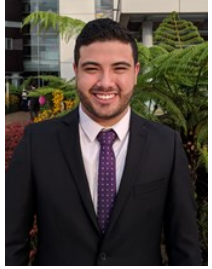
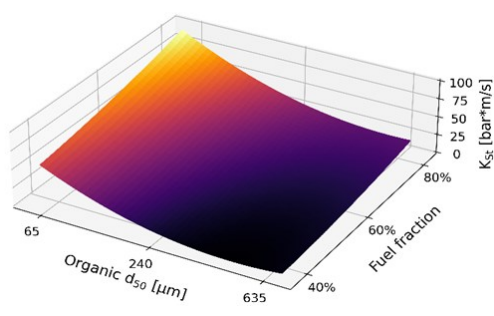
Optimizations are still necessary to further limit energy losses, i.e. increase the faradaic yield, while enhancing the elimination kinetics. Among the next steps proposed is the test on real effluent and the coupling of electrochemical processes.



Methodology :

Each blade acts as an electrochemical (micro)-reactor according to the inter-electrode distance (delec) applied. The purpose of this modular reactor is to obtain a set of cells which are combined to form a single macro-reactor, thus allowing the combination of several electrochemical systems in the same reactor. The reactor is made up of a tank with a rotating shaft that is capable of accommodating until four mixing blades (Fig. 1). The influence of several key parameters is being studied such as current density, delec, electrode materials and rotation speed.

References :

- [1] UNESCO, The United Nations world water development report 2019: leaving no one behind, UN Educ. Sci. Cult. Organ. (2019).
- [2] L. Rizzo, W. Gernjak, P. Krzeminski, S. Malato, C.S. McArdell, J.A.S. Perez, H. Schaar, D. Fatta-Kassinos, Best available technologies and treatment trains to address current challenges in urban wastewater re-use for irrigation of crops in EU countries, Sci. Total Environ. 710 (2020) 136312.

<p>2023</p> 	<p>Research subject: Dust explosion modeling: application to organic/mineral powder mixtures</p> <p>José Serrano (2nd year)</p> <p>Olivier Dufaud, Laurent Perrin</p> <p>PERSEVAL, TECALIMAN (Nantes – Club EMIX)</p>	
<p>Keywords : dust explosion, ATEX, powder mixtures, animal feed industry, process safety, risk assessment, modeling</p>		
<p>General context, scientific issues :</p> <p>The explosion risk assessment in the animal feed industry represents a challenge due to using powder mixtures (premix) with complex formulations and properties. Therefore, testing all possible operating configurations using standardized tests seems illusory</p>	<p>Illustration : organic/mineral powder mixture KSt versus organic PSD and fuel composition.</p>  <p>Main results</p> <p>The previous figure showed the significant non-linear effect of the organic powder's Particle Size Distribution (PSD) on the mixture's explosibility. In addition, the PSD of the mineral powder did not significantly modify the KSt values because of their fragmentation during the standardized test [1], which could lead to an overestimation of the inerting efficiency of these products. However, this variable became critical in estimating the mixture's MIE if its value was below a threshold for organic and mineral products [2]. On the other hand, the impact of the mixture composition followed a quasi-linear trend over the MIE and KSt values in the range studied for mineral products with an inerting mechanism based on radicals scavenging or low-temperature decomposition. Nevertheless, adding non-combustible products with reduced inerting capacity could improve the explosion kinetics of the mixture by improving its dispersibility and radiative heat transfer.</p> <p>The first model draft achieved consistent results, and its refinement with complex mixture data and inclusion of phe-</p>	
<p>Objectives and stakes :</p> <p>This research addresses the development of a model to predict the ignition likelihood (Minimum Ignition Energy – MIE) and explosion (deflagration index – KSt) safety parameters of organic/mineral powder mixtures commonly used in premix manufacturing to improve the implementation of the inherent safety approach and suitable prevention/protection measures in the animal feed industry.</p>		
<p>Methodology :</p> <p>The products used were selected along with the industrial partners considering their physicochemical properties and industrial relevance. An extensive parametric study has been conducted using the modified Hartmann Tube and the 20L Siwek Sphere based on the 14034/13821 European Standards for determining the ignitability and explosibility of pure and selected powder mixtures. The model construction is based on the significant factors found and adjusted to more complex scenarios. The gas products generated by an accidental explosion will be identified in further stages.</p>	<p>References :</p> <p>[1] Bu, Y., Amyotte, P., Li, C., Yuan, W., Yuan, C., & Li, G. (2021). Effects of dust dispersibility on the suppressant enhanced explosion parameter (SEEP) in flame propagation of Al dust clouds. <i>Journal of Hazardous Materials</i>, 404, 124119.</p> <p>[2] Yang, P. P., Meng, X., Zhang, Y., Liu, J. Q., Yan, K., Li, F., Wang, Z., Liu, Y., Dai, W. J., & Wang, Z. (2022). Experimental study and mechanism analysis on the suppression of flour explosion by NaCl and NaHCO₃. <i>Combustion Science and Technology</i>, 1–16.</p>	

<p>2023</p> 	<p>Research subject: Comparative evaluation of the potential recovery of strategic metals (Co, Ni) from old mine tailings</p> <p>Samuel Teillaud (2nd year)</p> <p>Lucie Coudert, Marie-Odile Simonnot, Marie Guittonny, Baptiste Laubie</p> <p>PERSEVAL, RIME</p>	
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Keywords : Mine tailings repurposing, cobalt, mineral processing, agromining, metal(loid) extraction, hydro-metallurgy, residues stability

General context, scientific issues :

Increasing demands of strategic and critical metals (SCM) such as Co and Ni, mainly used for rechargeable batteries, have encouraged countries to identify secondary sources of SCM. Repurposing of mine tailings seems to be a promising approach for both economical and environmental reasons [1].

Objectives and stakes :

This research project aims to compare two pre-concentration routes of Co and Ni from mine tailings while reducing their environmental footprints. Mine tailings were collected from different location in a legacy mine camp (ON, Canada). Mineralurgical processes combined with a chemical leaching or agromining will be developed, optimized (in terms of Co and Ni recovery) and compared (in terms of Co, Ni and As pre-concentration efficiency).

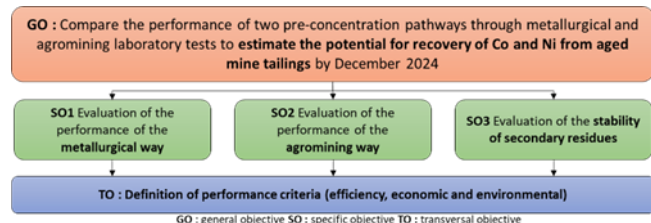
Methodology :

To achieve the objectives, physicochemical and mineralogical characterization of the residues have been conducted to better understand the potential of SCM recovery from mine tailings and define the most suitable preconcentration approaches (and their sequence) as well as the most relevant operating parameters.

The laboratory work will involve the use of various mineral processing separation processes, either combined or separately (e.g., gravity separation, size separation, magnetic separation, and flotation), sometimes preceded by pre-treatment steps to reactivate minerals' surface or increase the liberation of the minerals of interest.

Additionally, laboratory work focusing on the preconcentration of Co and Ni using hyperaccumulating plants will be carried out under controlled conditions to estimate their accumulation potential and assess the successful development of vegetation cover on such substrate through the production of aboveground biomass. To facilitate plant development, amendments, which were selected based on different criteria, will be mixed with the residues, and cultivation trials will be conducted under different conditions.

Illustration : Project objectives



Main results

The results showed that the selected mine residues were mainly composed of fine particles ($D_{80} = 50 \mu\text{m}$), contained 1310 mg kg⁻¹ Co, 943 mg kg⁻¹ Ni and 5245 mg kg⁻¹ As. Safflorite, skutterudite, cobaltite and erythrite, strongly altered and associated with silicate minerals (albite, quartz and chlorite), were identified as the main Co- and As-bearing minerals. The main Ni-bearing mineral identified was annabergite.


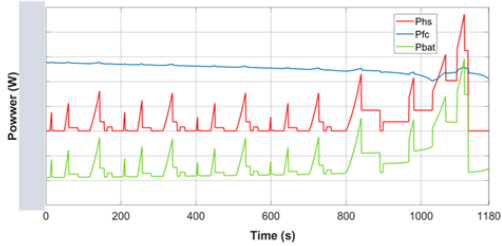
Preliminary experiments in mineral processing techniques (flotation) showed that the preconcentration of Co-bearing minerals is quite difficult (preconcentration factor of 1.2 to 2.5, recovery of 20 to 60%), while As-bearing minerals were a little bit concentrated (preconcentration factor of 1.2 to 3.5, recovery of 25 to 70%) using flotation. Preconcentration of Ni-bearing minerals remained relatively low.

The effectiveness of the flotation in separating targeted minerals from silicate gangue remains quite low, which can be explained by the complex mineralogy of mine tailings and hydrodynamic behaviour of particles. Germination rates were observed in *O. chalcidica* (74%) and *B. emarginata* (82%), while no germination was observed in *S. canadensis* and *P. arundinacea* under the given conditions (Petri dishes). To improve the properties of mining residues, different amendments (i.e., table compost and paper sludge) were tested. Based on phytotoxicity tests on *Lepidium sativum*, the paper mill sludge was not suitable due to insufficient maturation or possible toxicity. However, table compost seemed to be appropriate as it showed no phytotoxicity and provided favorable growth conditions. Therefore, table compost was used to enhance the structure and properties of the substrate. Germination rates on mine tailings varied depending on the species and the type of substrate used. For instance, germination rates of *O. chalcidica* varied from 0 to 40% depending on the proportion of amendment used.

Further modifications and alternative approaches are needed for improved preconcentration efficiency. Despite mixed results, promising collectors have been identified for cobalt preconcentration, and ongoing tests are underway to enhance efficiency.

References :

- [1] Falagán, C., Grail, B. M., Johnson, D. B. (2017). New approaches for extracting and recovering metals from mine tailings. *Minerals Engineering*, 106, 71-78. <https://doi.org/10.1016/j.mineng.2016.10.008>
- [2] Laubie, B., Vaughan, J., Simonnot M O. (2021). Processing of Hyperaccumulator Plants to Nickel Products. A. van der Ent et al. (eds.), *Agromining: Farming for Metals*, Mineral Resource Reviews. http://doi.org/10.1007/978-3-030-58904-2_3

<div> <div>2023</div> <div>LRGP</div> </div>	<div> <div> Research subject: Direct hybridization of a hydrogen fuel cell by batteries for a versatile, low energy suburban transport (HY2vers) </div> <div> Mengxi Wen (1st year) </div> <div> François LAPICQUE, Stéphane RAEL </div> <div> PERSEVAL </div> </div>	
<div> <div>Keywords :</div> <div>Proton Exchange Membrane Fuel Cell (PEMFC), Lithium-ion battery, Direct hybridization, Electric vehicles, Suburban transport</div> </div>		
<div> <div>General context, scientific issues :</div> <div> <p>Electric vehicles, either battery- or fuel-cell-powered, are a possible solution for a sustainable future due to their zero-emission characteristics. However, they tend to be heavy and costly, thus unsuitable for a wide range of urban and suburban personal transportation applications [1]</p> </div> </div>	<div> <div>Illustration :</div> <div>Simulation results for the power distribution of the hybrid source in one NEDC in the previous MSc work</div>  </div>	
<div> <div>Objectives and stakes :</div> <div> <p>The HY2vers project aims to model, design, and test at different scales a direct hybrid source between a Proton Exchange Membrane Fuel Cell (PEMFC) stack and lithium-ion batteries as the powertrain system for a lighter and cheaper electric vehicle dedicated to urban and suburban transportation. Coupling batteries with FC as an auxiliary power supply could compensate for the deficiencies of FC's slow response characteristics, absorb feedback energy generated by the engine during vehicle deceleration and braking, and thereby mitigate power fluctuations [2]. Direct hybridization also eliminates the need for a converter between these two, therefore reducing weight and cost.</p> </div> </div>	<div> <div>Main results</div> <div> <p>Previous MSc work demonstrated the feasibility of direct hybridization between a 100 cm² five-cell PEMFC stack (about 200W) and a lithium-ion battery (either LTO 40Ah or LFP 60Ah) as a hybrid source for urban and suburban vehicles, validated by both experiments and modeling based on the NEDC cycle for a fictitious vehicle weight [3].</p> <p>As exemplified in the figure, the fuel cell power PFC could be very stable during the NEDC driving cycle, which is to favor the fuel cell durability. On the other hand, for the two Li-ion batteries tested, the battery power Pbat can meet most of the transient demand of the hybrid source PHS, with the battery either accepting excess fuel cell power or adding insufficient fuel cell power [3].</p> <p>Further experiments on the new prototype hybrid source as well as model refinement for the simulation part need to be done in the following thesis work.</p> </div> </div>	
<div> <div>Methodology :</div> <div> <p>The thesis work will be conducted in two parallel parts: sizing and experimentation.</p> <p>1- Hybrid source sizing</p> <p>First, characterization tests of the 200 cm² 70-cell PEMFC stack (about 2.5kW) and lithium-ion batteries with different technologies (such as Lithium Iron Phosphate (LFP) and Lithium Titanate Oxide (LTO)) should be carried out using different techniques to obtain their physicochemical parameters. The latter will be used to construct electrochemical or equivalent circuit models. Based on the established models, the operation of the hybrid source will also be simulated in Matlab and Simulink to determine its characteristics, such as its performance or its flexibility in powering a fictitious vehicle in urban and suburban driving conditions (e.g., New European Driving Cycle).</p> <p>2- Experimentation</p> <p>Bench hybridization experiments will be performed to simulate the power distribution within the prototype hybrid source. The comparison of experimental data and simulation results will help to refine certain parameters and modify some model assumptions.</p> </div> </div>	<div> <div>References :</div> <div> <p>[1] M. HINAJE, "ANR-SHYBAH: Sizing HYdrogen fuel cell-BAtteries Hybridization." 2022.</p> <p>[2] S. Ma et al., "Fuel cell-battery hybrid systems for mobility and off-grid applications: A review," Renewable and Sustainable Energy Reviews, vol. 135, p. 110119, Jan. 2021, doi: 10.1016/j.rser.2020.110119.</p> <p>[3] M. Wen, "Direct hybridization between fuel cell and battery for suburban transport," ENSIC, LRGP-CNRS, Université de Lorraine, Master internship report, May 2022.</p> </div> </div>	





PRIMO

PROCESSES, REACTORS, INTENSIFICATION,
MEMBRANES, OPTIMIZATION



LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

<p>2023</p> 	<p>Research subject: CFD simulation of hydrodynamics and heat/mass transfer phenomena in membrane gas separation process</p> <p>Omar Abdul Majid (2nd year)</p> <p>Rainier Hreiz, Eric Favre</p> <p>PRIMO</p>	
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Keywords : CFD (computational fluid dynamics), Hydrodynamics, Membrane separation, Heat transfer, Mass transfer

General context, scientific issues :

Gas separation processes using membranes are gaining importance in industrial applications such as CO₂ capture, natural gas purification, ... especially after the introduction of new inorganic materials that offer high permeability and better resistance to harsh conditions such as high temperatures [1]. This requires the development of accurate models to accurately predict their performance.

Objectives and stakes :

The objective of this work is to create a non-simplified CFD model that includes all the coupled transfer phenomena in the inorganic gas permeation membranes, in order to improve the prediction of the performances of these processes, and to identify the capacities and limitations of the simplified 1D models [2]. In order to improve the assumptions used in the existing 1D models in order to obtain an acceptable accuracy with the re-

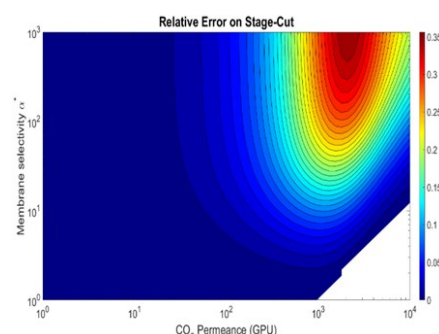
Methodology :

The commercial CFD code ANSYS Fluent is used for simulating the transfer phenomena inside a cylindrical membrane (hollow fiber membrane). The results of the CFD model are compared with experimental results found in the literature, and also with experimental results, done in the gaseous permeation unit in the LRGP laboratory. After validation, the results of this model are compared with the commercial code MEMSIC [2] in order to identify the capacities and limitations of classical models.

To reduce computational time, a new improved 1D model was developed by changing some hypothesis used in classical models and relying on the more fundamental relations for mass transfer coefficient calculation [3]. A comparison is done between the three models. This improved 1D model, is used to perform a kind of cartography to identify the operating conditions where concentration polarization occurs and its impact on the process performances, by calculating the error between the results of the classical model and those considering the phenomenon of concentration polarization.

At the end, the non-isothermal case that may occur in certain applications, mainly high-pressure feed flow, because of that, this case will be studied and modelled with CFD, and if possible added to the 1D model to benefit from its reduced computational time and its user-friendly environment.

Illustration : Relative error on stage-cut between considering and neglecting the phenomenon of concentration polarization



Main results

As explained before, and due to the axial symmetry in the hollow fiber membrane problem, a 2D CFD model to simulate the coupled transfer phenomena is done. The model is tested by comparison with theoretical results i.e. analytical solutions and experimental results. It is then used to develop the improved 1D model, which provides results within acceptable precision in comparison with CFD.

The results of the simulations will be tested with more experimental results produced in the gas permeation unit at the LRGP laboratory for the final validation of the developed models.

An exhaustive study on the impact of concentration polarization in membrane gas separation process is being performed for two main applications, post-combustion CO₂ capture and bio-gas purification.

A fine study of the effects of temperature change in gas separation using membranes will be done to evaluate the impact of Joule-Thompson phenomenon on the separation process.



To conclude, this CFD approach of gaseous separation processes will help us to better understand all the physical phenomena occurring during the process, and will provide more accurate simulation results in comparison with the previous models.

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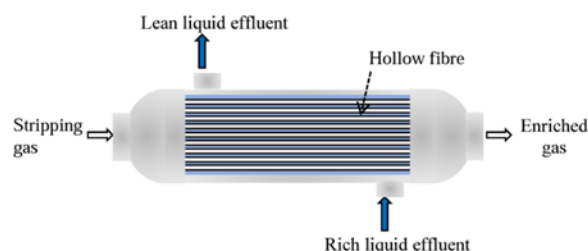
<p>2023</p> 	<p>Research subject: Hollow fiber membrane contactors for intensification of stripping operations: generic approach and application to water treatment</p> <p>Omar ALJASEM ALHMIEDY (1st year)</p> <p>Bouchra BELAISSAOUI, Sabine RODE</p> <p>PRIMO</p>	
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Keywords : Hollow fiber membrane contactor, intensification, stripping, modeling, volatile organic compounds.

General context, scientific issues :

In many industrial processes, volatile compounds, present in low concentrations in liquid effluents, have to be removed via stripping. This can be done using vacuum conditions or a carrier gas. The reference technology for stripping applications is the packed column. Hollow fiber membrane contactors are an alternative technology which offers potential process intensification opportunities. Indeed, they present significantly higher specific contact areas and mass-transfer coefficients. One of the challenges in the development of membrane contactors is their geometrical optimization, including fiber and module dimensions. In particular, prohibitive pressure drop as well as fluids maldistribution must be avoided for the two phases involved.

Illustration : Schematic diagram of the hollow fibre membrane contactor, stripping by a carrier gas



Objectives and stakes :

The thesis aims to develop a generic method for optimal design of hollow fiber membrane contactors in stripping operations. Indeed, each stripping operation is characterized by specific physicochemical and thermodynamic properties of both, the gas and the liquid phase. This leads to distinctive optimum operating characteristics, which, in turn, determine the choice of membrane material and structure as well as the optimal geometry.

Main results

The generic approach will allow to identify a priori the stripping applications for which the membrane technology offers a strong potential to intensify the process. In addition, it will be possible to link any application to the optimal design of the hollow fiber membrane contactor. If the intensification potential of the membrane technology is demonstrated, it will be validated on a pilot scale and can be extrapolated to industrial-scale use. Ultimately, this technology can offer an advantageous replacement for packed columns.

Methodology :

Different modeling approaches will be developed and compared, determining the required complexity level. Experimental validation will be performed on representative examples, especially regarding water treatment applications like deoxygenation and demethanization. The intensification potential of the technology will be quantified by estimating the volume reduction compared to packed columns.

References :

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- [3] P. Velasco, V. Jegatheesan, and M. Othman, "Modeling of hollow fiber membrane contactors (HFMCs) for the recovery of dissolved methane from anaerobic effluents," *Sep. Purif. Technol.*, vol. 286, p. 120488, Apr. 2022, doi: 10.1016/j.seppur.2022.120488.



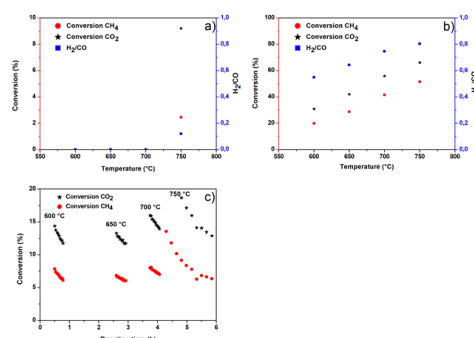
Keywords : heterogeneous catalysis, perovskites, kinetic, chemical reaction engineering

General context, scientific issues :

Dry methane reforming (DRM) is a reaction offering many environmental perspectives by valuing two greenhouse gases, CO₂ and CH₄, the main components of biogas. However, these molecules being very stable thermodynamically, the operating conditions are extreme, requiring very high temperatures varying from 700 to 1000 °C at atmospheric pressure.

Perovskites are promising catalysts for this reaction due to their stability and resistance to carbon deposition [1].

Illustration : Influence of temperature on catalyst SrZr_{0.5}Ni_{0.4}Fe_{0.1}O₃ a) Auto-Combustion, b) Pechini, c) Citrate



Objectives and stakes :

The first objective of this work is to make a comparison of the different synthesis methods described in the literature (Pechini, auto-combustion, and citrate) with a catalyst formulation of SrZr_{0.5}Ni_{0.4}Fe_{0.1}O₃ based on the work of Khazaal et al. [2]. These catalysts will be abbreviated SZ5NF5-P, SZ5NF5-AC, and SZ5NF5-C, respectively. Subsequently, the second objective is to determine the catalyst formulation that presents the best performance/stability ratio within a family of catalysts with the general formula SrZr(1-x-y)Ni_xFe_yO₃, where x varies from 0 to 0.6 and y from 0 to 0.15.

Methodology :

In this work, we analyzed substituted perovskites using several characterization techniques. X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX) were used to determine the crystalline structure and the elemental composition. Scanning electron microscopy (SEM), along with infrared and Raman spectroscopies were applied to determine the particle morphology and the chemical bonds. We used temperature-programmed reduction (H₂ - TPR) and temperature-programmed hydrogen desorption (H₂ - TPD) to study the reducibility of the catalysts and the surface nickel post-reduction. Finally, the BET analysis provided the specific surface area and material porosity.

Catalytic tests were conducted in a quartz tubular reactor. Catalysts were in situ reduced at 750 °C. A feed of N₂, CO₂, and CH₄ was then introduced into the reactor. The reaction temperature was maintained at different levels (600, 650, 700 or 750 °C) in initial tests, followed by a 23-hour stability test at 750 °C. Reactor outlet gases were analyzed with a gas chromatography-thermal conductivity detector (GC-TCD).

Main results


Dry methane reforming was explored in a series of catalytic tests varying reaction temperature, summarized in the figure for the different synthesis methods: a) Auto-Combustion, b) Pechini, c) Citrate. Catalysts prepared via the Pechini method demonstrated higher catalytic activity, with CO₂ and CH₄ conversion and H₂/CO ratio strongly influenced by the reaction temperature. The CO₂ conversion exceeded CH₄, which showed a minimum of 20 % conversion at 600 °C, increasing to 51 % at 750 °C. The H₂/CO ratio rose from 0.6 at 600 °C to 0.8 at 750 °C.

In contrast, the SZ5NF5-C catalyst showed lower reactivity and rapid deactivation from 600°C, attributed to coking and sintering of nickel particles. For the SZ5NF5-AC, no reactivity was observed despite similar TPR and TPD patterns than the catalyst prepared by the Pechini method.

For catalyst stability assessment, a 23-hour test was conducted at 750 °C. The results suggest good catalyst stability throughout the testing period, with slight deactivation towards the end potentially due to carbon deposit or sintering.

References :

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- [2] Khazaal, Majida H.; et al., Enhanced Methane Reforming Activity of a Hydrothermally Synthesized Codoped Perovskite Catalyst, *Energy & Fuels*, 2018, 32, 12826–12832.

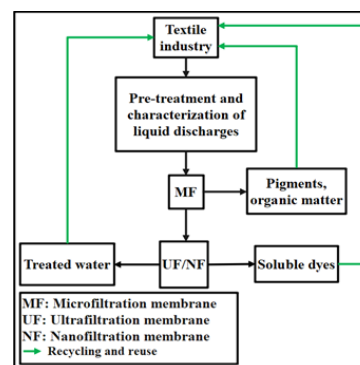
<p>2023</p> 	<p>Research subject: Geomaterial-based composite membranes for textile wastewater nanofiltration: fabrication, testing and process design</p> <p>Zakarya, Chafiq Elidrissi, (1st year), International Cotutelle PhD, Hassan II University of Casablanca (Morocco) and Lorraine University (France))</p> <p>Bouchra Belaisaoui, Sabine Rode, Mohamed Ouammou, Brahim Achiou</p> <p>PRIMO</p>	
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Keywords : Geomaterials, Composite Membrane, Nanofiltration, Dyes, Modeling, Design, Textile Wastewater.

General context, scientific issues :

Textile industries generate huge amounts of liquid effluents loaded with pollutants such as dyes, pigments, heavy metals, and other toxic products. Membrane filtration using geomaterial-based composite membranes is a promising low-cost, green separation technology. However, their design is challenging [1].

Illustration : Proposed treatment process for textile wastewater.



Objectives and stakes :

This thesis aims to develop low-cost and sustainable composite membranes from local Moroccan geomaterials (pozzolan, kaolinite, clays, etc.), in order to design an efficient process for the removal and recovery of dyes from textile wastewater.

Main results

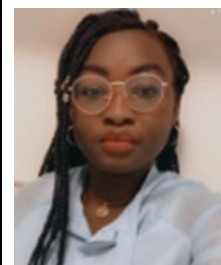
The main expected result is the fabrication of low-cost geomaterial-based composite membranes with competitive performances. The membranes performance will be assessed experimentally. Secondly, we aim to model and to optimize the nanofiltration process. The key parameters are the physical and the chemical structure of the membrane and the operating conditions; namely flow rate, transmembrane pressure, temperature and feed composition. Particular attention will be given to prevent fouling. Finally, technico-economic and environmental analyses will be conducted in order to assess the industrial relevance of the process.

Methodology :

Firstly, selected local geomaterials will be used in order to fabricate flat and tubular ceramic microfiltration membranes. Secondly, two-dimensional nanomaterials will be synthesized and deposited on the microfiltration support membrane as a selective layer, thus creating a composite membrane for nanofiltration applications. The application of fabricated membranes in the treatment of textile wastewater adopting the approach is presented in Figure 1. Finally, the modeling of transport phenomena within the prepared membranes will be carried out in order to understand the involving mechanisms and to identify optimal operating conditions and to prevent fouling.

References :

- [1] Y. Dong, H. Wu, F. Yang, S. Gray, Cost and efficiency perspectives of ceramic membranes for water treatment, *Water Res.* 220 (2022) 118629. <https://doi.org/10.1016/j.watres.2022.118629>.



Keywords : reverse osmosis, membrane, permeability, simulation, model

General context, scientific issues :

Population explosion and human industrial activities have been causing huge consumption of water resources and water pollution. Power generation plants, in particular, nuclear power plants, produce liquid effluents that must be treated for disposal or recovery. Membrane technologies are regarded as the most powerful tools for addressing these issues because they enable the supply of high-quality water at a low cost and energy consumption [1].

With this vision, Melusine, a joint research team between researchers from EDF R&D and LRGp, was set up to conduct studies on the evaluation and development of liquid and gaseous effluent treatment processes in nuclear power plants using membrane technologies.

The technology used in this study is reverse osmosis, which is well-known for its performance in salt rejection and water permeation [2]. Its efficiency depends on a number of factors including operational parameters, employed membrane, feed water characteristics and particularly, concentration polarization. This phenomenon is due to an accumulation of rejected solutes near the RO membrane surface and can be limiting for the process.

Illustration : Reverse osmosis unit



Main results

The results of this study are classified as confidential.

Objectives and stakes :

The main objective of this research is to evaluate the performance of industrial unit modules by acquiring experimental data (flowrate, composition, temperature, pressure). Those parameters will be implemented in home-made simulation tools able to predict separation performances for different operating conditions and design industrial plants. Those simulation tools will be particularly useful in process synthesis methodologies process aimed to conceive optimised process architecture potentially based on different separation technologies (reverse osmosis, membrane distillation, thermal processes...)




Methodology :



The experiments are carried out with a fully designed reverse osmosis pilot at LRGp in order to determine the operating parameters of the study. Retentate and permeate characteristics are measured for different feed solute concentrations and the liquid samples, collected and analyzed via Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) or titration with mannitol.

The experimental results (permeabilities of the different components of the system) obtained will then be implemented in the developed simulation tools based on mass balances and permeability laws [3].

References :

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- [3] MELUSINE. Projet : Procédés membranaires pour le traitement d'effluents liquides dans le domaine de l'énergie.

<p>2023</p> 	<p>Research subject: C2FUEL : Carbon Captured Fuel and Energy Carriers for an Intensified Steel Off-Gases based Electricity Generation in a Smarter Industrial Ecosystem</p> <p>Eglé Ferreri (research engineer)</p> <p>Eric Favre, Christophe Castel</p> <p>PRIMO</p>	
<p>Keywords : membrane contactor, carbon capture and storage (CCS), CO₂ capture demonstrator, chemical absorption, post-combustion CO₂ capture</p>		
<p>General context, scientific issues :</p> <p>C2FUEL project aims to develop energy-efficient, economically and environmentally viable CO₂ conversion technologies. This concept will be demonstrated at Dunkirk at DK6 power plant. Main goal is to develop, integrate and validate processes at industrial-relevant scale for the conversion of captured CO₂ from off-gases in fuel (DME).</p>	<p>Illustration : CO₂ capture demonstrator designed by LRGP for C2FUEL project</p> 	
<p>Objectives and stakes :</p> <p>LRGP has been involved in numerous projects in this field: CICADI[1] and AMELIE[2] validated the concept of membrane contactor for CO₂ absorption at the lab scale on key chemical solvents; EnergiCapt[3] and C2B[4] projects involved the upscaling and its validation on real flue gas. Results shown in each case high intensification potential compared to conventional contactor. Thanks to its expertise, LRGP is responsible of developing a carbon capture and conditioning demonstrator unit.</p>	<p>Main results</p> <ul style="list-style-type: none"> i) A method has been developed to assess, through one experiment, both thermodynamics and mass transfer data based on a batch to continuous approach. The set-up can easily be used for studies of membrane and solvent performances, and allowed to obtain quickly key data of several solvents commercial HFMCs. Work presented during Euromembrane 2021, ECCE/ECAB 2021 and SFGP 2022. (ii) On site experimental campaigns with a mobile pilot unit have proven the effectiveness of a polymethylpentene HFMC and MEA solvent with real flue gas over 1000hr. Key pre-treatment technologies for removal of sulphur compounds and dust were also validated by attaining CO₂ purity and trace compounds requirements. (iii) Both lab-scale and pilot-scale unit results were correctly predicted by a 1D absorption model. (iv) Design of the demonstrator unit was performed, and construction by PIGNAT SAS has ended on April 2023. Delivery is expected for July 2023. The demonstrator will run for 5000hr to assess the reliability of membrane contactor for CO₂ absorption with real complex fumes in an industrial environment 	
<p>Methodology :</p> <p>CO₂ present in flue gas (blast furnace gas) produced by Arcelor Mittal steel factor and routed to DK6 power plant, needs to be selectively captured, purified and sent in catalytic reactors. Purity requirement is high and will be achieved by implementing a chemical absorption process using hollow fiber membrane contactors (HFMC). HFMC consist in a gas-liquid contactor where hollow fibers act as an interface between the flue gas and the absorption solvent.</p> <p>LRGP contribution consist of 4 steps: (i) Development of a lab-scale CO₂ absorption unit used to assess compatibility and performances of a selection of absorption solvents and several HFMC; (ii) Design, construction and commissioning of a fully instrumented mobile semi-industrial absorption and regeneration pilot plant, in order to assess impacts of real flue gas complex composition; (iii) Validation of an ab initio tailor-made 1D isothermal model of CO₂ chemical absorption by experimental results, to provide final design of the demonstrator unit; (iv) Design of a CO₂ capture demonstrator according to experiments and modelling</p>	<p>References :</p> <ul style="list-style-type: none"> [1] Chabanon, Roizard, et Favre, « Membrane Contactors for Postcombustion Carbon Dioxide Capture » [2] Makhouloufi et al., « Ammonia Based CO₂ Capture Process Using Hollow Fiber Membrane Contactors » [3] « Project CO₂ EnergiCapt » [4] « Project C2B » 	

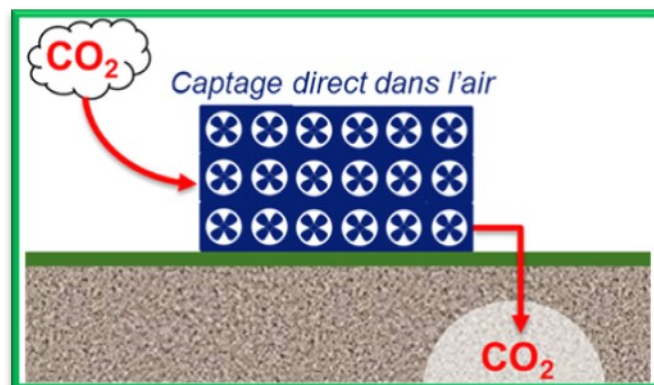
<p>2023</p> 	<p>Research subject: Integration of Direct Air Capture (DAC) in a low-carbon system.</p> <p>Paul de Joannis de Verclos (1st year, PhD) Christophe Castel , Olivier Authier , Eric Favre PRIMO, EDF</p>	
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Keywords : Direct Air Capture, DAC, CO₂, Simulation, Carbon Dioxide Removal, Process

General context, scientific issues :

There has been a recent and growing interest in the Direct Air Capture (DAC) technology because of its potential to decarbonize and achieve carbon neutrality. This negative emission technology capture CO₂ from the atmosphere and then stored it almost permanently or convert it to valuable product.

Illustration : Remove CO₂ from the atmosphere with Direct Air Capture.



Objectives and stakes :

Today, direct air capture technologies are developing rapidly but still present many technical and economic uncertainties. The main objective is to evaluate DAC process architectures, from technical and economic points of view, based on the main techniques for CO₂ separation from ambient air by means of modelling and numerical simulation.

Main results

No original results were obtained yet. A literature review was carried out to study the four separation techniques mentioned above. This research highlighted three main players who are developing prototypes and demonstrators with different technologies: Climeworks (adsorption - demonstrator - TRL 7), Global Thermostat (adsorption) and Carbon Engineering (absorption - prototype - TRL 6). Current capture costs are in the order of \$200-1000 per tonne of CO₂ captured depending on the technology and economic assumptions. The aim is to get below \$100 per tonne over the next decade. However, many uncertainties remain regarding the development of these technologies. Work to verify the physico-chemical parameters of a CO₂ capture model with monoethanolamine under Aspen plus has been undertaken and is still ongoing.

Methodology :

The approach is to first study separate DAC technologies based on four separation techniques - absorption, adsorption, membrane and electrochemistry - and then to study hybridisations of technologies to improve performance. These DAC processes will be studied on a commercial scale and for integration into a low-carbon energy production system. Modelling, simulation and economic analysis will be used to assess the overall and techno-economic performance.

Two absorption DAC processes - monoethanolamine and potassium hydroxide [1] absorption - will be simulated via Aspen Plus. Adsorption will be studied with the particle bed adsorbent "Lewatite VP OC 1065" [2] and a monolithic adsorbent to be defined through simulation in Aspen Adsorption. Membrane separations will be simulated with the MEMSIC tool. Finally, an electrochemical process [3] will be simulated using MATLAB. All processes will be evaluated economically with the Aspen Process Economic Analyzer tool.

References :

- [1] Keith, David W., Geoffrey Holmes, David St. Angelo, et Kenton Heidel. 2018. « A Process for Capturing CO₂ from the Atmosphere CE ». *Joule* 2 (8): 1573-1594. <https://doi.org/10.1016/j.joule.2018.05.006>.
- [2] Schellevis, Michel. 2023. « CO₂ Capture from Air: A Process Engineering Approach », avril. <https://doi.org/10.3990/1.9789036555852>.
- [3] Voskian, Sahag, et T. Alan Hatton. 2019. « Faradaic Electro-Swing Reactive Adsorption for CO₂ Capture ». *Energy & Environmental Science* 12 (12): 3530-3547. <https://doi.org/10.1039/C9EE02412C>.



Keywords : Preparation process, bio-based Elastomer, rubber Composites, damping Performance, hydrogen bond

General context, scientific issues :

Vibration and noise not only have harmed people's physical and mental health, but also seriously affected on the stability and reliability of mechanical equipment operation. Among numerous methods of vibration and noise reduction, the preparation of polymer damping materials with excellent performance is one of the important solutions because their viscoelastic properties can absorb vibration mechanical energy and dissipate it as heat energy.[1-3] The loss tangent ($\tan\delta$), defined by the ratio of loss modulus (E'') to storage modulus (E'), can be a measurement of the dissipation of the vibration energy.[4] High performance damping materials should have a high loss factor ($\tan\delta > 0.3$) over a broad temperature range of at least 60-80°C difference. [5] The damping properties of the rubber materials are determined by their inherent hysteresis loss which increases with the increase of the internal friction between molecular chains. There has been little research on environment-friendly polymer damping materials. Recently, bio-based itaconate elastomer was synthesized by environmentally benign emulsion polymerization of bio-based dibutyl itaconate with butadiene, which has curable double bonds and many side ester groups attached to the polymer backbone. And this new bio-based polymer has been found exhibiting good physical and damping properties.[6,7] However, this kind of homopolymer usually only has effective damping performance below the room temperature with a narrow temperature range of 20–30°C, which is difficult to meet the requirements. Therefore, the preparation of bio-based elastomer composites by blending and modification method with high loss factor at room temperature and wide temperature range damping is an extremely important and challenging issue.

Objectives and stakes :

- (1) Clarify the damping mechanism by studying the relationship between the microstructure and properties of bio-based elastomers;
- (2) Elucidate the damping mechanism and influencing factors of bio-based elastomer composites by blending it with other rubbers, nano-fillers or organic small molecules, etc.;
- (3) Provide theoretical guidance and design principles for the development of new bio-based elastomers with high damping performances

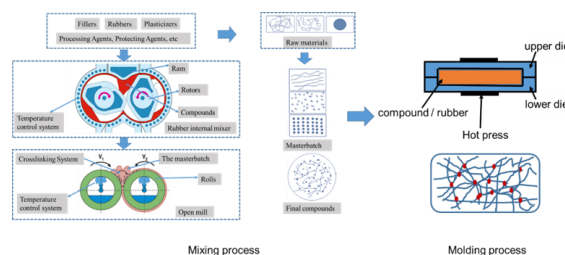
Methodology :

Based on the blends ratio 60/40 of NR/PDBIBG composites, incorporating the epoxidized natural rubber with different amounts were prepared by internal mixer in order to improving strength and damping performance. The contributions of the crosslink network and the dispersion of fillers in different phases to damping properties will be studied.

Formulation for filled rubber compound: rubber 100 (PDBIBG/NR/ENR 40/30/30, 40/40/20, 40/50/10, 40/60/0), ZnO 5.0, stearic acid 2.0, carbon black N330 40.0, antioxidant 4010NA 1.5, antioxidant RD 1.5, paraffin wax 1.0, accelerator DM 1.0, accelerator CBS 0.5, sulfur 1.5.

The raw rubber was masticated by an RM-200C HAPRO torque rheometer (Harbin HAPRO Electric Technology Co., Ltd., Harbin, China) at 80°C and 70 rpm for 1 min. Then stearic acid, zinc oxide, paraffin wax, antioxidant 4020 and antioxidant RD and half of the amount of the carbon black were added and mixed for 2 mins. After that, the half of the carbon black was added and mixed for another 1 min. The ram was lifted and the masterbatch was mixed for 2min and discharged below 125°C, stored at room temperature for 30 min. Afterward, the masterbatch, sulfur, accelerator CBS and DM were added into the torque rheometer at 70°C and 70 rpm and mixed for 3 mins. The resulting compound was discharged below 105 °C and then put in an open mill (Farrel Corporation, the United States) at 50°C. The roll distance was adjusted to 0.6mm for making a triangle bag 3 times, and then adjusted to 2mm to make a sheet. After being rested at room temperature for 24 h, the rubber blends and filled rubber compounds were cured at 160 °C for optimum curing time ($t_{90} + 3$) min under 10 MPa with a RCM NP24-100 T4CE type Automatic Operation Vulcanizing Press (Jinlun Technology Co., Ltd, Hong Kong, China).

Illustration: Preparation of vulcanizates



Main results

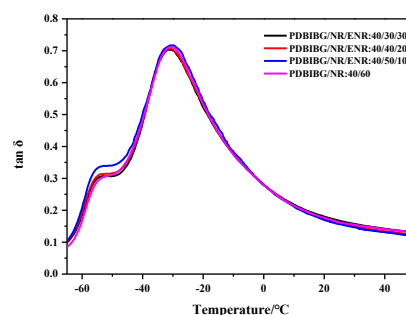


Figure 1. $\tan\delta$ versus temperature curves of the NR/PDBIBG composites

Figure 1. shows the $\tan\delta$ versus temperature curves of the filled NR/PDBIBG composites. With the introduction of ENR, the loss factor $\tan\delta$ is increased, and the damping temperature moves to a higher value, and the damping temperature range is wider than that of NR/ PDBIBG blends. When the amount of ENR is 10phr, the damping temperature range is from 51 to 60°C, indicating that ENR can broaden the damping temperature range of PDBIBG.

References :

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Keywords : microfluidics, modelling, mass transfer, liquid-liquid extraction, kinetics, uranium

General context, scientific issues :

Reactive liquid-liquid extraction is commonly used to purify effluents and recover desired substances, such as uranium and plutonium in the nuclear field's PUREX process. TBP, the current organic solvent, has drawbacks that complicate the recovery process [1, 2]. To address this, researchers are exploring new extractants, like monoamides, which show great potential [3, 4]. However, understanding extraction kinetics is crucial to assess their performance and industrial viability.

Objectives and stakes :

Several conventional equipments are reported in the literature for the investigation of the kinetics in liquid liquid extraction systems. Nevertheless, such techniques are not suitable for studying systems with fast chemical kinetics. Recently, there has been an increased interest in microfluidic devices due to their mass transfer performances. Thus, this work aims to determine kinetic rate constants of uranium extraction by several extractants using an approach coupling microfluidic devices and mass transfer modeling.

Methodology :

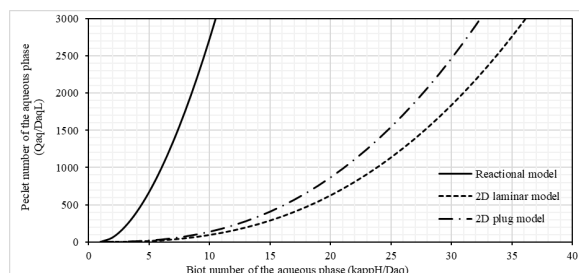
The initial phase of this study involved analyzing kinetic data obtained from a previous PhD thesis. The chemical system under investigation was that of uranium extraction from a nitric acid media by TBP diluted in TPH. The Kinetic data were acquired using a parallel flow microfluidic setup. Various phenomenological models were thus developed, each increasing in complexity. These models included a simple analytical model considering only the chemical reaction kinetics, a 2D plug model incorporating diffusion perpendicular to the interface, a 2D laminar model, and a 3D laminar model where diffusion in both directions perpendicular to the flows is considered.

The second part of the work focused on conducting a sensitivity analysis of the developed models. The aim was to identify the most suitable model for investigating the kinetics based on the specific experimental conditions applied.

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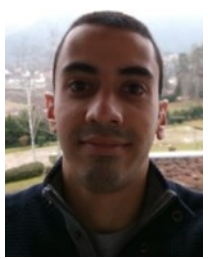
Illustration : Variation of the relative error of the obtained value of the apparent rate constant using the simple models with that obtained using the 3D model for different Peclet and Biot numbers



Main results

The analysis of the kinetic data for the fast chemical system (U(VI): HNO₃/ TBP:TPH) indicated that a chemically limited regime was obtained at a high initial concentration of uranium (119 g.L⁻¹) due to Marangoni convections. Indeed, these interfacial turbulences seem to eliminate the resistance due to diffusion. Nevertheless, for low initial concentrations of uranium (10-30 g.L⁻¹) and short residence times in the microchannel (< 13 ms), both diffusion and reaction limit the mass transfer. The obtained value of the apparent rate constant under current operating conditions ([HNO₃] = 3 M, % TBP = 30 % (v/v)) was of $(7.2 \pm 2) \times 10^{-4}$ m.s⁻¹. This value is much higher than what conventional extraction techniques predicted, indicating the better mass transfer efficiency in the microfluidic setup due to the decrease of the diffusional limitation.

The sensitivity analysis results highlighted the Peclet and Biot numbers as crucial parameters for determining the apparent rate constant. These dimensionless numbers represent the ratio between diffusion and advection time (Peclet) and the ratio between diffusion time and reaction time (Biot). The figure depicted demonstrates that the simple analytical model has a limited range of validity. It can be reliably used for systems with a characteristic reaction time five times faster than the diffusional time, provided the Peclet number exceeds 500. The faster the chemical system, the higher the required Peclet number (i.e., flow rate). In contrast, both the 2D plug and laminar models exhibit comparable performance

<div> <div>2023</div>  </div>	<div> <div>Research subject: Up-flow boiling of a zeotropic mixture in an offset strip fins heat exchanger</div> <div>Nassim Khirouni (post-doctoral researcher)</div> <div>Laurent Falk, Jean-Marc Commenge, Kaijun Koh, Thomas Pourbaix, Thibault Plays</div> <div>PRIMO, Air Liquide</div> </div>	
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Keywords : Flow boiling, zeotropic mixture, offset strip fins, heat transfer coefficient, pressure drop

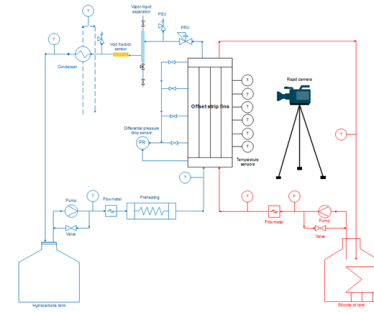
General context, scientific issues :

The shift towards zero-carbon emission energy systems is a paramount step to resolve the problem of climate change and pollution. One of the viable solutions is the use of hydrogen, however there are still some technical challenges facing the development of big scale infrastructure. Hydrogen liquefaction is currently viewed as the best option for the transport and storage of this energy vector to enable its expansion. Nevertheless, liquefaction processes consume a lot of energy and need to be optimized, especially in the case of hydrogen where it is required to reach temperatures below 80 K [1] [2].

Gas liquefaction is often achieved using cryogenic mixed refrigerant processes, where different types of heat exchangers can be used. Among them is the offset strip fins heat exchanger known for its large surface area in a compact volume [3]. In these processes, liquefaction is performed by combining multiple steps of heat exchange and different mixtures of refrigerants. The composition of refrigerants mixture is considered the most flexible parameter as it affects the overall process performances. The mixture can contain up to 9 components and in some cases the components are chosen to obtain multiple immiscible liquid phases [4] [5]. A better understanding of the flow boiling of refrigerants mixture in heat exchangers is a topic of extreme interest as it allows determining the operational variables that are of influence and establishing proper correlations for design purposes.

Although the flow boiling of mixtures in simple geometries such as tubes [6] and plate heat exchangers [7] have been reported in the literature, only two studies have investigated the flow boiling of a mixture in an offset strip fins heat exchanger [8] [9]. This shows the importance of this work in order to generate more data and help optimize performances.

Illustration : Simplified representation of the studied experimental pilot



Methodology :

As mentioned above, the experimental pilot will have the same structure as the previous work [10]. The test section is to be composed of three parts held together by a casing:

A glass for flow visualization using a rapid camera;

An offset strip fins passage for the flow boiling of the hydrocarbon mixture, placed underneath the glass;

An offset strip fins passage for the flow of the hot fluid (silicone oil) that is in contact with the previous passage to ensure the heat exchange.

The two fluids (hydrocarbon mixture and silicone oil) flow upwards through the offset strip fins passages in closed loops using pumps and the flow rates are controlled by flowmeters. The rapid camera is to be placed in front of the glass.

Before going inside the heat exchanger, the hydrocarbon mixture exiting the tank at a precooled state is preheated to a temperature close to the mixture's bubble temperature of about 5°C. This allows reserving the offset strip fins passage for the evaporation of the mixture. Multiple temperature sensors are to be used to assess the temperature of the mixture at the inlet, throughout the length of the passage and at the outlet. The pressure drop of the mixture at different levels of the heat exchanger is to be measured using a differential pressure drop sensor. After exiting the heat exchanger, the mixture passes by a condenser to return to the precooled liquid state. To operate at high pressures, a pressure relief valve (PRV) and a pressure safety valve (PSV) are to be placed at the outlet of the heat exchanger. Before the condenser, it would be convenient to perform the composition measurements of each phase and to place the void fraction sensor; the latter systems are still being studied. Given the fact that the mixture is composed of hydrocarbons there is a risk of flammability. For that, a purging system using nitrogen is to be placed to ensure that the lower limit of flammability is avoided in the storing tank and the test section.

The silicone oil loop is much simpler as the fluid does not undergo a phase change. Temperature sensors are to be placed only at the inlet and outlet of the hot fluid passage. A simplified representation of the pilot is given by the illustration.

Using the temperatures, pressure drop and composition measurements it is expected to be able to experimentally evaluate the two-phase heat transfer coefficient, the two-phase pressure drop and the vapor quality. The footage of the rapid camera should give us an indication of the flow regime, which would be useful to establish a flow map. If successful, the measurement of the void fraction will help complete the hydrodynamic study. The experimental data could lead to proposing correlations for transfer coefficients that are more adapted for the flow boiling of mixtures in an offset strip fins heat exchanger.

Objectives and stakes :

This study is an experimental work that focuses on the up-flow boiling of a binary mixture (zeotropic mixture) in an offset strip fins heat exchanger. The mixture of interest is composed of hydrocarbons and considered as a model fluid of the mixture used in reality. The experimental pilot is expected to allow the visualization of the flow regimes and to measure the two-phase heat transfer coefficient and the two-phase pressure drop. In addition, it is desired to work under similar conditions as those encountered in the industry, mainly in terms of the mass flux of the mixture per unit area, the exchanged heat flux per primary surface and the dimensions of the offset strip fins. Also, the experiments are to be performed under different pressures (< 5 bar). This work comes as a continuation of a previous experimental study [10] that investigated the evaporation of water in channels, and aims to reuse some of the equipment already available. The design of the pilot must also take into consideration some operational limits such as the maximum temperature and pressure tolerated, the length of the heat exchanger and flammability risks linked to the evaporation of hydrocarbons.

A system to separate phases at the outlet of the heat exchanger and to measure the composition of each phase is being studied. As found from the mass balance, the composition allows to have an experimental estimation of the vapor quality. A dynamic phase separation can be achieved using a T-junction that would be simple to put in place. Finally, a capacitance sensor to measure the void fraction of the two-phase flow at the outlet of the heat exchanger is also being studied. Assessing this parameter is important for the characterization of the two-phase flow and to calculate other factors such as the slip ratio. It should be noted that two-phase flows are complex and performing experimental measurements could reveal to be tricky.

Main results

The pilot still under design, no experimental data have been generated yet. It is difficult to predict the results in advance given the novelty of the subject

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Keywords : Membrane gas separation, Zeolites, Molecular dynamics (MD), Grand Canonical Monte Carlo (GCMC)

General context, scientific issues :

Membrane-based processes are widely used for the separation of various gas mixtures (CO₂/CH₄, CO₂/N₂). Zeolite membranes show good, high permeability and selectivity (Zito et al., 2017). However, the mass transport mechanisms are complex and their quantification is challenging.

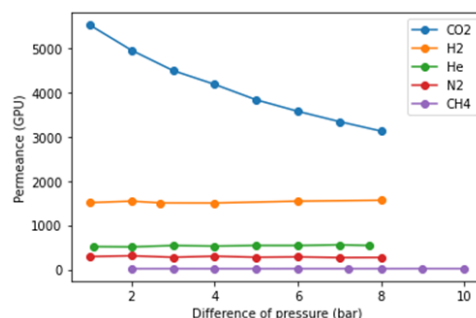
Objectives and stakes :

This work aims to evaluate the efficiency of porous zeolite membranes for gas separation through a multi-scale study coupling macroscopic and microscopic levels. The experimental approach allows the determination of the membrane performance, while the molecular simulations provide an atomistic insight into the transport phenomena. The data obtained from the GCMC and MD simulations integrated into simple 1D transport models to predict zeolite membrane properties.

Methodology :

- Experimental measurements of membrane permeance (P) and selectivity (α) using a chabazite tubular membrane. Different operating conditions (Q, T, P, composition) are tested for the separation of pure gases (CO₂, CH₄, N₂, O₂, He, Ar, H₂) and mixtures (CO₂/CH₄, CO₂/N₂).
- Numerical simulations at the molecular level (MD and GCMC). Adsorption isotherms, diffusion coefficients or permeances are predicted by atomistic calculations. The results will be compared with experimental data. The predictive potential of molecular simulation will be evaluated.
- Modelling of mass transport phenomena in porous media using well-known equations from the literature (van den Bergh et al., 2010). The mechanisms involved are represented, leading to the estimation of the adsorption and diffusion parameters.

Illustration : Permeance of pure gases at 25 °C as a function of the pressure difference between the feed and permeate sides, measured for a CHA SSZ-13 membrane



Main results

The laboratory results with a high performance chabazite membrane show that the permeance of different pure gases depends on several factors, such as: (i) preferential adsorption of CO₂, as its permeance is not constant and decreases with Δp ; (ii) molecular sieving effects - molecules with larger kinetic diameter have lower permeance, such as CH₄, whose diameter is similar to the pore openings (3.8 Å).

Adsorption isotherms have been calculated up to 1100 kPa for all studied gases at 5 different temperatures (273, 298, 318, 343 and 373 K) using GCMC. Henry and Langmuir model parameters were fitted and selectivities were calculated. The simulation show a good prediction accuracy: the predicted ideal adsorption selectivity for CO₂/CH₄ mixture at 298 K is 4.5 (all-Si CHA membrane), while the value reported in the literature is 5 (Pham and Lobo, 2016).

Molecular dynamics simulations are performed to have a deep insight into the molecular scale interactions and to determine microporous diffusion coefficients. Future work is to obtain the permeance directly from NEMD simulations.

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Keywords : Membrane separation process, simulation, energy, thermodynamics

General context, scientific issues :

Membrane separations are a key technology in gas separation, with an easy steady-state operation. Nevertheless, it has been theorized¹ that operating under an unsteady state could increase separation performances. Different possible implementations have been studied for this purpose²⁻⁴.

Objectives and stakes :

The objective of this research is to study an innovative implementation of simultaneous compression-separation steps, operating in an unsteady mode and with a focus on energy consumption minimization. Technically, the head of a piston compressor containing a gas mixture to be purified is equipped with a membrane, which allows progressive compression as well as separation.

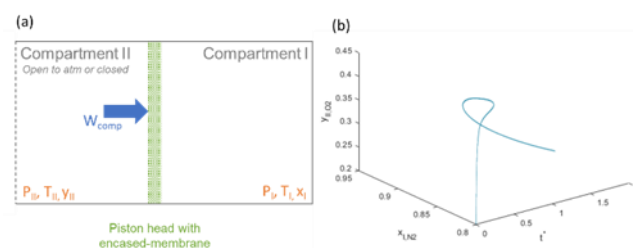
Methodology :

- Using a parametric study, a comparison is realised between the energy demands of membrane-piston system with two operating modes (open and closed) and a steady-state operation system. It aims to identify the scenarios where the unsteady mode could offer better performances (separation efficiency and energy requirements). Additionally, a dimensional study is carried out to establish interesting dimensionless parameters to describe the system and help the design of the units

References :

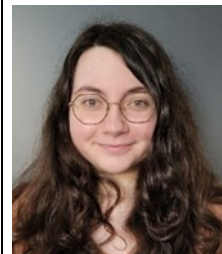
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Illustration : (a) schematic representation of the membrane-piston (b) composition path for a set of dimensionless number in closed-mode for a O₂/N₂ mix



Main results

Preliminary findings show that, in certain cases, the membrane-piston system can achieve the same separation performance with less work when compared to a steady-state at identical exit pressure. It is important to mention that the steady-state system requires a compression of the retentate, as the membrane-piston system enables a high-pressure recovery for the corresponding compartment. Several dimensionless parameters, in particular a permeation number and a thermal number in addition to the selectivity, have been identified as key factors controlling the system. They help to determine the range of variables that make the membrane-piston system advantageous. As depicted on figure (b), the composition path, represented by the variation of $x_{N_2,I}$ and $y_{O_2,II}$ (plotted on dimensionless time) for a fixed set of dimensionless parameters is highly similar for every design tested. This means that the same performances can be achieved for different membrane as long as the dimensionless parameters are kept identical. To validate the model and simulation results, an experimental setup is currently under conception and construction at the LRGP workshop.



Keywords : CFD, Entropy generation minimization, Intensification, Optimal design, Second law analysis, Simulation

General context, scientific issues :

To face the challenges of global warming, improving energy system efficiency is essential. However, non-optimal reactors/systems designs lead to an overuse of energy and resources and thus, to systemic irreversibility. Minimizing this entropy generation is a major issue for energy transition, requiring a global approach to reduce primary energy consumption [1].

Objectives and stakes :

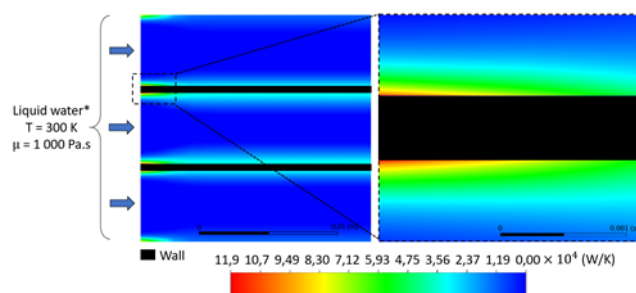
The goal of the present work is to improve the efficiency of reactor-exchangers by minimizing irreversibilities through optimization of their design as well as heat integration of the converter. The developed methodology is applied to a plug flow reactor with a direct heat exchange system, both operating under laminar flow conditions. It aims at determining the optimal geometric profiles of the reactor and associated heat exchangers, i.e., those allowing to achieve minimal entropy generation in the system. This dynamic optimization strategy will be applied using both 1D models and CFD modeling approaches and validated through controlled experiments [1].

Methodology :

Firstly, entropy generation in the process is evaluated through the two modelling approaches used in the literature. The first approach is the global approach [2], which relies on mixing properties to calculate the total entropy production thanks to entropy balances. The local approach [3] calculates entropy production in each cell of the mesh, which allows a 3D mapping of entropy production within the reactor. The global approach is computationally less demanding compared to the local approach, but have a lower precision.

Secondly, a numerical optimization of the reactor-exchanger will be carried out for the hydrolysis of acetic anhydride reaction, using both 1D and CFD approaches, in order to determine the optimal configuration. Once this design is established, a pilot unit will be set up to compare its performance in terms of irreversibility with that of the reference geometry and to confirm the energy savings that it allows achieving.

Illustration : Viscous dissipation entropy production profile (W/K) (left) with a zoom on one of the internal walls (right)



* The fluid properties were taken identical to those of liquid water, except for a deliberate increase in viscosity to highlight the entropy production.

Main results

Both local and global strategies for entropy generation calculation were implemented under Matlab (1D systemic modelling approach) and Ansys Fluent (2D CFD modelling) software. Three main sources of entropy generation were identified and their calculation matched between the local and global computation strategies:

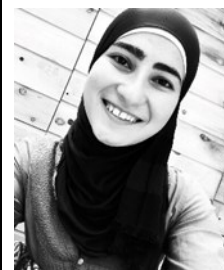
- Viscous dissipation, whose driving force is pressure gradient
- Heat transfer, which occurs when there is a temperature inhomogeneity
- Chemical reaction, which is represented by a gradient of chemical potentials

On the other hand, a comparison between CFD and the systemic modelling approaches highlighted the limits of 1D models which were shown to lead to significant underestimation of the irreversibilities.

The next step is to optimize the plug flow reactor using the CFD software Fluent. Dynamic optimization will be carried out using Bejan's method of minimizing entropy generation [4]. The local reactor-exchanger radius (which will be discretized following a Control Vector Parametrization strategy) as well as the steady-state operating conditions will be used as optimization variables. The identified optimal design will be 3D-printed and experiments will be carried out to confirm the validity of the numerical results.

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Keywords : membrane separation process, helium, process synthesis, simulation, permeance, selectivity

General context, scientific issues :

Helium is an indispensable resource carrying critical issues for the future, being now a strategic resource vital for many industries (lifting, leak detection, electronics, cryogenics...). [1] At a time when 100% of European helium is imported at high-energy costs and carbon footprint, 45-8 Energy is the first company in France developing an eco-friendly local helium short circuit supply chain using membrane technology, which could therefore significantly reduce the environmental impact of such industry. Promet-Hé is an innovant project elaborated by 45-8 Energy in collaboration with the EMSP team at the LRGP.

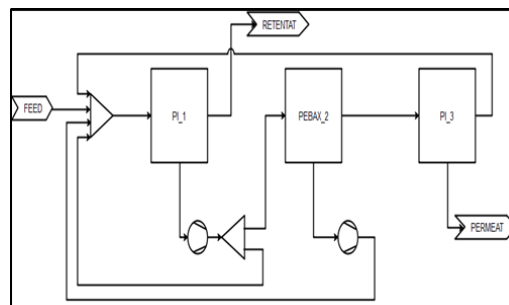
Objectives and stakes :

Helium is an indispensable resource carrying critical issues for the future, being now a strategic resource vital for many industries (lifting, leak detection, electronics, cryogenics...). [1] At a time when 100% of European helium is imported at high-energy costs and carbon footprint, 45-8 Energy is the first company in France developing an eco-friendly local helium short circuit supply chain using membrane technology, which could therefore significantly reduce the environmental impact of such industry. Promet-Hé is an innovant project elaborated by 45-8 Energy in collaboration with the EMSP team at the LRGP.

Methodology :

To obtain a good separation performance, it is necessary to choose judiciously the membrane materials, the architecture of the process and the operating conditions as well. Experimental tests for pure gases were carried out first at the LRGP to measure permeance data of several commercial modules at different temperatures and pressures. MEMSIC, a developed software at LRGP for simulating multi-constituent separation through a gas permeation membrane separation, is then used for parametric studies and to simulate the membrane separation process for mixtures depending on the operating conditions (Pressure, Temperature, Flow rate, compositions, etc...). [2] The experimental data for mixtures were compared with simulation results to verify the accuracy of selective and separation performances specially at high stage cuts zones. A process synthesis methodology has been carried out to optimize the architecture of the membrane separation process through a cost objective function, allowing multi-stage membrane architectures. The objective of this pre-study is to study the main principles of design and sizing of the process and assess their robustness as well. These outlines will be discussed later on with the equipment manufacturer in charge of pilot construction.

Illustration : Optimization results from experimental permeability data of different tested modules





Main results

For He/N₂ separation, it is possible to have access to materials with high selectivities and exhibiting good permeabilities. It's the case including polyimides, some of which are commercially available (e.g.: UBE). Some permeances of the module UBE obtained experimentally at different temperatures are presented in the table below. Meanwhile, He/CO₂ couple, has a particularity: it is possible to have access to materials selective to He (selectivity He/CO₂ >1) or selective to CO₂ (He/CO₂ selectivity < 1) but the performance of commercial materials is quite low with few materials with selectivities greater than 10 or less than 0.1. By elsewhere, some non-commercial materials show interesting selectivities. The experimental obtained results were compared with those reported in the literature. The part of design, simulation, parametric studies and optimization of the membrane purification process were approached with the experimental collected data. The first results using process optimization clearly show the interest of a multi-tiered architecture using different types of membranes. The targeted helium purity and recovery rate constraints are accessible.

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<p>2023</p> 	<p>Research subject: Methodology for systematic process design: analysis of superstructural and generative approaches</p> <p>Antonio Rocha Azevedo (1st year)</p> <p>Jean-Marc Commenge, Romain Privat</p> <p>PRIMO, EDF</p>	
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Keywords : Process synthesis, Process Systems Engineering, Superstructure, Generative approaches, Optimization

General context, scientific issues :

Process synthesis describes the search for optimal process conception (i.e., determination of optimal flow-sheet and corresponding operating conditions). Two process synthesis approaches will be benchmarked: superstructure-based optimization [1] and so-called generative methods [2]. They will be applied to the design of energy-conversion processes and reaction-separation processes.

Objectives and stakes :

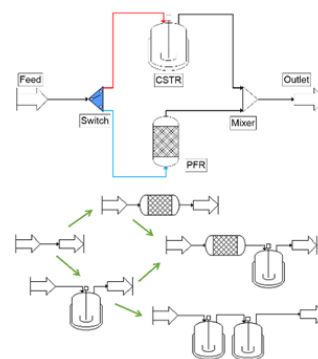
This thesis' objective is thus to compare the different process synthesis approaches (evaluating their advantages, limits, and inconveniences) and propose a methodology that answers constraints emerging from current social issues. We can cite as such constraints: the integration and modelling of uncertainties; time variability; and the coupling of different modelling approaches (simulators and black-box).

Methodology :

The first process synthesis approach considered in this work involves postulating a set of process structures and integrating them in a large flowsheet called a superstructure. For a given process, the definition of the superstructure is a key question that will be addressed first. A process simulator is used for implementation of the superstructure, and optimization is done through a direct-search algorithm.

Although superstructure allows for the simultaneous optimization of both the structure and continuous variables, this method can only determine the optimal structure if it is contained in the superstructure. In order to get around this limitation, generative approaches – that do not limit the structural search space – will be considered too. In these methods, process alternatives are generated through evolutionary algorithms (e.g., the ab-initio evolutionary approach [3]) or machine learning methods. In the former, a population of flowsheets is mutated iteratively, until the yielded process alternatives are no longer improved. In the latter, a neural network is trained to generate flowsheets like in a Natural Language Processing task; the generation of good flowsheets is targeted through Transfer Learning approaches [4].

Illustration : Superstructural vs evolutionary approach



Main results

Development of general synthesis methodologies combining the different synthesis approaches, as well as derivations and guidelines according to the problem type, objectives, and issues. For example, applications involving different sources of uncertainty will require different modelling and resolution approaches. Processes involving variability will require flexible solutions. Although a more general methodology may be devised, it must be adapted to the characteristics of different problems.

Optimal designs will be proposed for energy conversion processes such as the supercritical CO₂ Brayton cycle as well as for other processes that will be defined later.

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Keywords : waste, thermal treatment, modelling, simulation, process supervision

General context, scientific issues :

Incineration is a common waste disposal technique, thanks to its versatility, volume reduction capability and the energy recovered. Despite its overall simplicity and robustness, the heterogeneity of the waste and local phenomena make it a process that is hard to model and control.

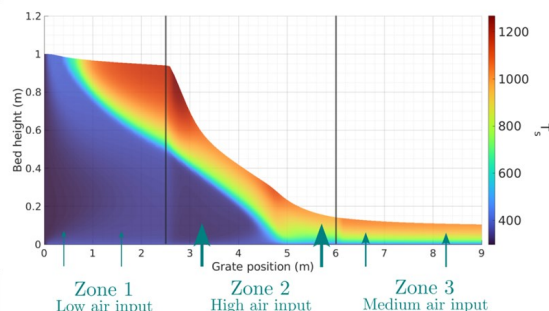
Objectives and stakes :

The essence of this research project consists in modelling the main process of an incinerator, from waste feed to stack, in a manner that is performant enough to be used to follow real-time a real plant, even when operational conditions are not steady and even when uncertainty is high. The goal is to obtain non-measured physical values but that are relevant for the monitoring, operation, and maintenance of the incinerator

Methodology :

One of the specific features of the incineration process is the concentration of sensors towards the end of the process, at the stack [1]. Thus, it appears very beneficial to model the entire process to validate the model against the online measurements made on the EVNA incinerator operated by SUEZ in Schweighouse-sur-Moder. The units are first modeled separately: waste pit, feed system, kiln, boiler, acid scrubbing, bag-house filters and induced-draft fan; each partially validated. Special attention is given to the kiln where the heterogeneous porous medium combustion is the combination of numerous multi-scale phenomena [2]. Once all the units are modelled, the whole process model may be validated against the EVNA plant.

Illustration : Solid temperature distribution of a simulated waste bed. The grate and primary air injection parameters are taken from the incinerator of Schweighouse-sur-Moder (France) operated by SUEZ.



Main results

For the waste modelling, an adaptation of scientific description and industrial practice for waste characterization was setup using data from various literature sources [3].

For the kiln, a waste bed model has been developed using a custom variant of the finite volumes and the so-called “walking-columns” approach. The following main phenomena:

- solid mixing induced by the grate
- solid shrinking
- thermal radiation, conduction, and convection
- homogeneous and heterogeneous reactions

are all considered but using quite simple sub-models. This allows the developed model to be more complete than existing control models that typically neglect some uneasy phenomena about the solid phase but simpler and more usable than behaviour models used for instance as a base to study pollutant speciation. The code developed can produce waste bed representations (see illustration) and combustion outputs including dynamic responses with calculation times well under real time.

References :

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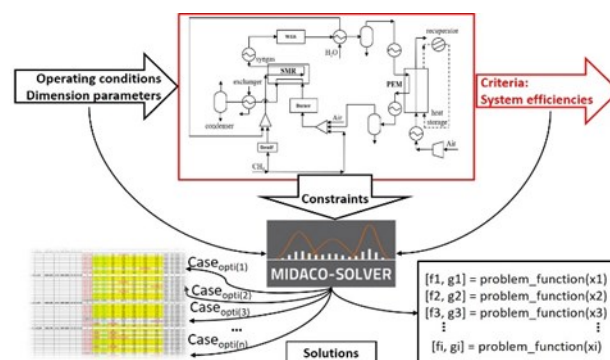


Keywords : Micro-Combined Heat and Power, process intensification, multicriteria optimization, fuel partialization

General context, scientific issues :

In view of the energy transition in the buildings sector, several successive thermal regulations have been implemented (i.e. RE2020 [1]). The micro-cogeneration system (μ -CHP) based on the fuel cell is considered to be a relevant solution for transforming chemical energy into electrical and thermal energy, to meet the proposals of RE2020.

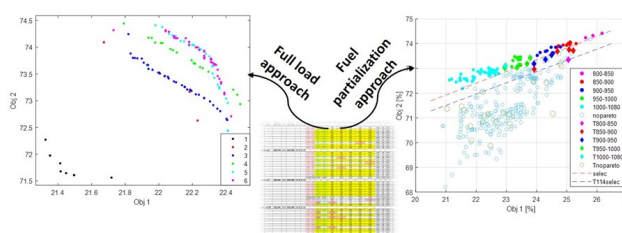
Illustration : System optimization construction.



Objectives and stakes :

The main objective of this study is to develop a μ -CHP process based on the fuel cell with the integration of a millistructured reactor-exchanger. In this context, the approach aimed firstly to build a compact reactor-exchanger model, and then to integrate the model into the complete process. Finally, various optimization strategies were implemented to identify the optimum conditions by considering of objective functions: net electrical efficiency and thermal efficiency.

Main results



Methodology :

In order to optimize the system operating conditions while catering for specific thermal and electrical load profiles, two types of Pareto fronts were identified as a function of the different operating modes of the fuel cell, represented by the terms of "full load" and "fuel partialisation". Due to numerical difficulties associated with the reactor-exchanger simulation module (CO-Prosec), the Pareto fronts were determined by assembling a large number of converged simulations and selecting the non-dominated optimum points which satisfy the given constraints.

The data was analyzed in the domain of decision variables to identify the optimum operating conditions at fixed power, as well as the modulation strategies required to provide continuously optimal behavior under variable electrical power conditions.

References :



[1] Réglementation environnementale RE2020. <https://www.ecologie.gouv.fr/reglementation-environnementale-re2020> (accessed 2022-08-22).

The optimization has been carried out with an external optimization algorithm (MIDACO-SOLVER) to handle MINLP problems. The Pareto fronts obtained from "full load" approach represent the result of collecting data from different optimizations by changing the optimizer parameters and the ranges of decision variables. Comparing the Pareto fronts obtained from the complete optimization (cases 5 and 6) and those obtained from the data collection, it can be observed that the Pareto fronts obtained from the complete optimization are slightly better than the others cases (1-4). Although the data collection method from different optimizations has been applied, it is not quite suitable for the exploitation of the studied area. The different ranges of variable electrical power have been applied in "fuel partialization" approach as inequality constraints. The Pareto fronts obtained from the latter have been determined by using a linear function (selec). The result shows higher level of compatibility for higher values of electrical power with the complete optimization case study (diamond points).



BIOPROMO

BIOPROCESS, BIOMOLECULES

<p>2023</p> 	<p>Research subject: Multiscale modeling of a monoclonal antibody production bioprocess for its optimal control</p> <p>Alejandro AVILAN GARZON (2nd year)</p> <p>Eric OLMOS, Bruno EBEL, David PFISTER</p> <p>Bioprocesses, Biomolecules, BioProMo, Ypso-Facto</p>	
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Keywords : Modelling, Bioprocess, Antibody, Chinese Hamster Ovary cells, CHO

General context, scientific issues :

Monoclonal antibodies (mAbs) represent nearly 50% of the therapeutic protein market and are mostly produced via the CHO cell line [1]. Efforts to improve performance, robustness, and controllability to automate these production processes include the development of digital twins to simulate, test, and predict the system behavior quickly and at low cost [2]. However, this requires models, ranging from the microscopic (intracellular mechanisms) to the mesoscopic (bioreactor hydrodynamics) that would be capable of integrating all the process data necessary for the quantification and prediction of performance indicators [1].

Objectives and stakes :

This work will integrate experimental kinetic monitoring of CHO cultures producing monoclonal antibodies and the development of microscopic and macrokinetic models. The information collected at the microscopic scale as well as the experimental data will allow to better understand the intracellular dynamics during the culture and to propose and/or improve mechanistic and/or statistical macrokinetic models

Methodology :

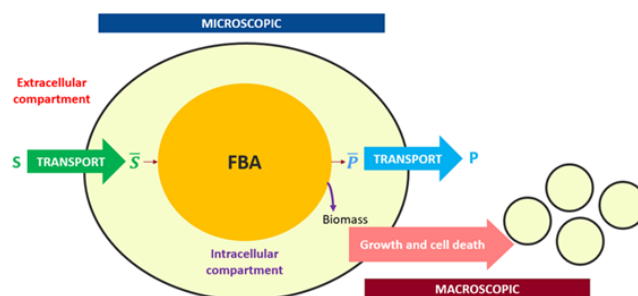
Experimental data: Collection of experimental kinetic data of CHO cell cultures in batch and fed-batch cultures carried out in Erlenmeyer flasks and Ambr STR bioreactors through measures of extracellular and intracellular metabolite concentrations.

Microkinetic modelling: Modelling the distribution of intracellular fluxes and intracellular metabolism validated by the previous experimental data.

Macrokinetic modelling: and/or statistical macrokinetic models to predict the impact of changes in culture conditions (substrates and product concentrations, T, pH, DO) in cell growth, substrates consumption and production rates.

Real-time piloting: Evaluation of the predictive relevance of the models built by estimating and correcting culture trajectory in real time to optimize process piloting

Illustration : Scheme of the multiscale model developed in the PhD



Main results



Intracellular and extracellular kinetic data of cell cultures of CHO producing monoclonal antibodies were generated at the scale of Erlenmeyer (25 mL). The results showed that amino acids such as glutamine, asparagine and cystine, were the first substrates to be depleted suggesting that those amino acids are limiting substrates in batch cultures. More data expected to be generated using different culture conditions to capture different phenomena and to expand the validity range of the developed models.

With the aim of create a kinetic model that respects the atomic and mass balances, the basis of an atomistic kinetic model using intracellular and extracellular concentrations was established. The preliminary results show that the model can accurately predict cell growth, substrates consumption and production rates in batch and fed-batch cultures.

Preliminary microkinetic simulations (FBA) of internal flux distribution were made using the obtained experimental data. These first results coupled with both literature and experimental data will allow to better understand the intracellular metabolism of CHO cells, and to improve the microkinetic metabolic model

References :

- [1] Frenzel, A., Hust, M., & Schirrmann, T. (2013). Expression of recombinant antibodies. In *Frontiers in Immunology*. 4, 217.
- [2] Kyriakopoulos, S. et al. (2017) 'Kinetic modeling of mammalian cell culture bioprocessing: The Quest to advance biomanufacturing', *Biotechnology Journal*, 13(3), p. 1700229. doi:10.1002/biot.201700229

	<p>Research subject: Screening, separation and identification of metal-chelating peptides in protein hydrolysates</p> <p>Jairo Andrés Camaño Echavarría (2nd year) Laetitia Canabady-Rochelle, Katalin Selmeczi</p> <p>BIOPROMO, L2CM</p>	
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Keywords : protein hydrolysate, screening, metal-chelating peptides, fish processing by-products, agro-industrial byproducts, Tilapia scale, Sunflower meal

General context, scientific issues :

Bioactive peptides, naturally encrypted within protein sequence under an inactive form, are released upon proteolysis. These peptides have gained great interest due to their numerous biofunctional activities e.g., antioxidant, antihypertensive, antimicrobial, and metal-chelating [1].

Objectives and stakes :

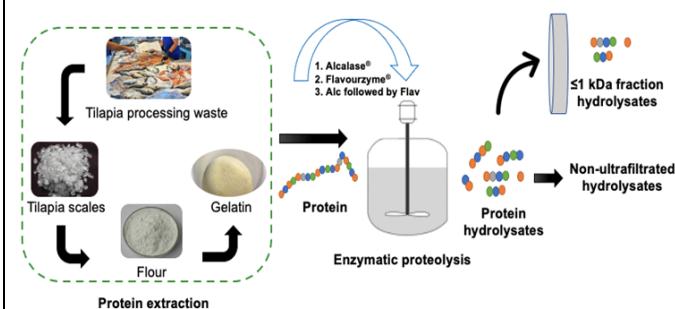
This PhD thesis aims to investigate the use of two by-products, i.e., red Tilapia scale and sunflower meal - for the production of peptide hydrolysate after their protein extraction and the discovery thereof of metal-chelating peptides (MCPs) by setting up UV-spectroscopy, surface plasmon resonance (SPR), switch-SENSE®, and immobilised metal affinity chromatography (IMAC) as screening and separation techniques. In a second aim, link between SPR and IMAC will be used for further chromatography modelling and simulation by studying several peptide sequences of interest found in Tilapia scale and sunflower proteins.

Methodology :

Red Tilapia (*Oreochromis* spp.) scales and sunflower meal by-products were used to produce protein isolates (PI) by a hydrothermal extraction and isoelectric precipitation, respectively. Then, the PI were used to produce hydrolysates using enzymes (Alcalase®, Flavourzyme® and Protamex®) used alone or sequentially. The hydrolysates were ultrafiltrated onto 1 kDa membrane and characterized for their degree of hydrolysis (DH), peptide concentration, molecular weight distribution, metal-chelating activity, radical scavenging activity, reducing power, antimicrobial and antihypertensive activity.

On the other hand, based on a theoretically screening approach, several peptide sequences of interest present in these two resources were selected by a software currently under development at LRGP, from the main proteins found in red Tilapia scale (i.e., Type I collagen) and sunflower protein (11S globulin). The sequences were submitted to a theoretical hydrolysis and 1kDa ultrafiltration. Retained peptide sequences were classified according to their ability to complex Ni²⁺ or Cu²⁺ based on HSAB theory [2]. The potential MCPs sequences screened theoretically were synthesized (by external company) and investigations for their metal-chelating properties using IMAC are currently under optimization while acting on various parameters such as NaCl concentration, elution method, peptide concentration and type of column.

Illustration : Experiment set up to produce bioactive peptides from Tilapia scale by-product



Main results

Upon the extraction, the protein content initially present in Sunflower meal (46.10 %) and Tilapia scale (40 %) increases up to 90.90 and 95 % in the protein extracts respectively, fulfilling the requirements of protein isolate in terms of protein content (>90%). Concerning the Tilapia scale gelatin hydrolysates, although Alcalase® followed Flavourzyme® hydrolysate showed the highest degree of hydrolysis, the highest biofunctional properties were found unexpectedly in Alcalase® one, therefore sequential hydrolysis seems not to improve the investigated hydrolysate properties for this protein resource. According to IMAC experiments, the peptides sequences obtained from theoretical hydrolysis of Tilapia scale gelatin tend to exhibit high retention times, meaning a strong metal-binding properties compared to those produced from sunflower protein hydrolysis. Taken together IMAC results, 16 studied peptides containing at least 1 His on their sequences show an expected behavior according to the theoretical hydrolysis and complexation, whereas 4 peptides characterized were by a low or no retention time, indirectly correlated to metal chelating properties. The different levels of metal ions affinity might be related to the number and position of His on the sequences.

References :

- [1] Liu et al., 2020. Trends Food Sci Technol. 96: 199-207
- [2] El Hajj et al., 2021. Application in nutrition: mineral binding. In F. Toldra (Ed.). 455–483



Keywords : Biocatalysts, enzyme production, extrusion, Nylon 6,6; elastane; textile recycling

General context, scientific issues :

More than 130 million pairs of nylon tights (better known as "pantyhoses") are sold each year in France. In general, these tights are ephemeral products. The complex composition of tights makes it difficult to reuse components such as nylon and elastane. A closed-loop recycling process consisting of remaking tights from used ones would allow us to break out of this linear "produce, consume, throw away" model.

Objectives and stakes :

The main objective of this project is the development of a green process for the hydrolysis of Nylon 6,6 which is one of the main polymer's component of tights. This study will include a laboratory scale experimental work on the selected processes (thermomechanical and enzymatic) in order to separate Nylon 6,6 and elastane. Hydrolases enzymes will be used for the enzymatic hydrolysis of Nylon 6,6 and elastane.

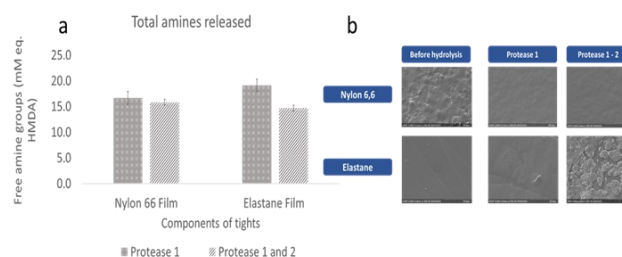
Methodology :

A first approach will be focused on the understanding of the hydrolysis mechanisms of Nylon 6,6 and elastane catalyzed by commercial and microbial enzymes. The production of oligomers constitutive from Nylon 6,6 will be the key to select the optimal conditions of the various treatments implemented.

At this stage, some of commercial proteases are used to study their specificity and performance against Nylon 6,6 and elastane. Also, the production of another enzyme from fungi is considered to hydrolyze the ester bonds of elastane. Enzymatic extracts are evaluated in order to develop a recycling process. The surface enzymatic hydrolysis of polyamide and elastane textile fiber (film and yarn) are measured.

The hydrolysis reactions are monitored by derivatization of primary amino groups which are established by the o-phthalaldehyde assays (OPA) [1] and the residual solid material will be characterized with scanning electron microscopy (SEM). Also, the changes of chemical structures are studied by spectroscopy infrared (FT-IR). Thermal analyses such as differential scanning calorimetry (DSC) are carried out in order to measure the degree of degradation in the amorphous phase of the polymer [2]–[4]. In a second approach, a thermal pretreatment is considered in order to degrade the elastane. Afterwards, the coupling of thermomechanical and enzymatic treatments will be considered.

Illustration : Performance of commercial enzymes for Nylon and elastane films a) Quantification of amines released, b) SEM images of the Nylon 6,6 and elastane films after enzyme hydrolysis



Main results

In this study it is expected to develop an appropriate combined process using thermo-mechanical and enzymatic systems in order to obtain the main raw material of Nylon 6,6. Commercial enzymes have demonstrated the ability to hydrolyze amine functions, showing on the one hand an activity towards both fibers, however, there is no particular specificity either for polyamide or elastane. On the other hand, a more important surface degradation after hydrolysis was observed in elastane than in Nylon 6,6 by scanning electron microscopy (SEM) as it is shown in the illustration (b). Also, it is observed that enzymes obtained from fungi can degrade the surface of elastane. Enzymes more specific to Nylon 6,6 are currently being evaluated. Hence, others studies are in progress for the separation of polyamide and elastane. In fact, these fibers have different physicochemical properties which makes it difficult to create a recycling process. So, polyamide can be modified by amorphization in order to decrease the crystallinity index and increase the hydrolysis rate of the enzymatic attack.

References :

- [1] C. Silva et al., Biocatal. Biotransformation, 2004, 357–360.
- [2] A. Magnin et al., Methods Enzymol., 2021, 317–336.
- [3] A. Eberl et al., J. Biotechnol., 2009, 207–212.
- [4] F. Di Bisceglie et al., Polymers, 2022, 411.

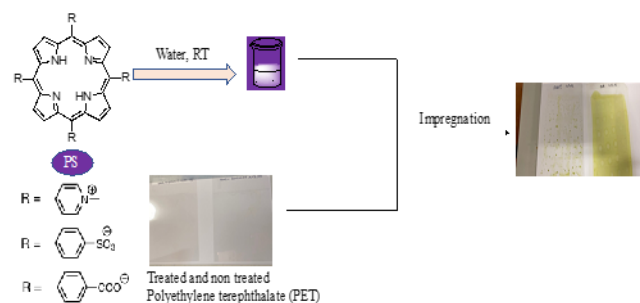
<p>2023</p> 	<p>Research subject: Development of new anti-microbial materials for hygiene and food safety</p> <p>Tatevik Chilingaryan (4th year)</p> <p>Dr. Céline Frochot, Dr. Benoit Habermeyer</p> <p>BIOPROMO</p>	
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Keywords : Photodynamic inactivation, Photosensitizer, Singlet oxygen, Bacteria, Virus

General context, scientific issues :

Many people suffer from diseases caused by bacteria. Conventional antibiotics are no more efficient, and new methods such as Photodynamic Inactivation of bacteria (PDI) are necessary¹. The important advantage of PDI over traditional antibiotics, is that the same photosensitizer is capable to destroy viruses, bacteria, yeasts, fungi and protozoa². Another advantage PDI over conventional antibiotic treatment is that no microbial resistance has been reported so far. PDI is a combination of photosensitizer (PS) and light to generate cytotoxic reactive oxygen species (ROS) that kill bacteria and viruses.

Illustration : Fabrication of antimicrobial films



Objectives and stakes :

Our goal is the development of new antimicrobial films based on porphyrinoids, for application in hygiene and food safety. The objective consists in several steps such as synthesis of PS (porphyrins, phthalocyanines and chlorins), study of Influence of counteranions and symmetry on electrochemical properties of water-soluble porphyrins. Incorporation of PS into polymer film and their photophysical studies³.

Main results


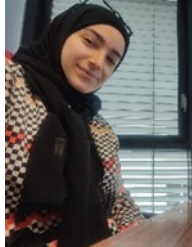
- Synthesis of second-generation photosensitizers
- Intercalation of PS into inorganic materials
- Investigation of photophysical properties of host@guest materials⁴
- Incorporation of PS into polyethylene terephthalate (PET)
- Photophysical properties of PS, PS+film have been investigated.
- Singlet oxygen production for some of PS+film have been confirmed

Methodology :

- Synthesis of photosensitizers
- Characterization by UV-Vis, MS, HPLC phase normal and reverse phase, ¹H RMN, Fluorescence and Singlet Oxygen production measurements.

References :

- [1] B. Habermeyer, T. Chilingaryan, R. Guillard, J. Porph. And Phthalocyanines, 2021, 25, 359-381.
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- [4] T. Chilingaryan, A. Schlachter, C. Frochot, B. Habermeyer, P. D. Harvey, R. Guillard, J. Porph. and Phthalocyanines, 2023.

<p>2023</p> 	<p>Research subject: Nanoparticles to optimize the effects of radiotherapy of brain tumors: multiscale modeling and experimental validation RXNanoBrain</p> <p>Batoul Dhaini (post-doctoral researcher)</p> <p>Céline Frochot</p> <p>BIOPROMO</p>	
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Keywords : Glioblastoma, nanoparticles, peptide, radiotherapy

General context, scientific issues :

Glioblastoma multiforme (GBM) is the most common and aggressive primary brain tumor in adults, characterized by an extremely poor prognosis. It remains particularly difficult to treat because of the intrusive penetration of isolated cells into adjacent tissues. The standard treatment for patients with newly diagnosed GBM is maximal surgical resection followed by postoperative radiotherapy with concomitant and adjuvant therapy with temozolomide. Radiotherapy consists of a total dose of 60 Gy for 6 weeks using external beams of megavoltage X-ray photons. Antitumor activity is based on the generation of secondary electrons and free radicals in oxygen-rich environments, responsible for cellular damage such as single and double strand DNA breaks, membrane lipid peroxidation and oxidation proteins. However, external photon beam radiation therapy is nonspecific because a large dose can be delivered to healthy tissue along the path of the photons, anterior and posterior to the tumor area and the doses needed to eradicate the tumor cells are too large to be considered well tolerated by the surrounding healthy brain tissue, including the risk of necrosis of normal brain tissue. Treatment options at the time of recurrence include reoperation, repeat radiation therapy, systemic therapy, or combination therapy [1]. In this unfavorable context, we also pointed out that interstitial photodynamic therapy (iPDT) could appear as an alternative strategy likely to reduce recurrences [2].

Objectives and stakes :

The RXnanoBRAIN project aims to validate the preclinical proof of concept of an nanoparticle conjugated to peptide, enabling dual-modality tumor imaging (MRI and CT) and radiation dose enhancement, additionally targeting the NRP-1 receptor overexpressed by cells in the GBM tumor microenvironment. (1) We will demonstrate that these nanoparticles are highly compatible with current CT-guided radiotherapy and emerging MRI-guided approaches, (2) how these functionalized nanoparticles combined with radiotherapy can reduce proliferation, migration and cell invasion capacity of GBM cells, (3) how tumor selectivity, intracerebral distribution (vascular, interstitial space) pre and post irradiation and tumor residence time of nanoparticles can consolidate the rational foundations of the fractional irradiation.

References :

- [1] Mann et al, Front. Neurol. 2017, 8:748.
- [2] Bechet et al, Cancer Treat Rev. 2014, 40:229-41.

Methodology :

The methodology and experimental approach consists of:

- 1- Design and characterization of functionalized nanoparticles. We will design and characterize a novel theranostic nanoparticle for dual-modality (MRI and CT) contrast enhancement and clinical radiation dose amplification. The objective of this WP is the production and optimization of ultrasmall nanoparticles targeted by peptide and its characterization.
- 2- Clinical requirements. CT & MR contrasts. New radiotherapy techniques such as IGRT will offer clinicians a unique opportunity to improve local control without increasing treatment toxicity by sparing normal tissues.
- 3- Selectivity & Biodistribution. Through the imaging properties of our multifunctional theranostic nanoparticles (Gd for MRI, Bi for CT and fluorophore for fluorescence if necessary for experimental approaches), we will document their behavior at the cellular level (cellular uptake by a method ICP-MS validated for quantification of total Gd and Bi in cellular samples and subcellular localization by confocal fluorescence microscopy), at the tissue level (tumor selectivity, residence and vascular diffusion using a brain tumor window model) and at the level of the whole organism (organs of accumulation, residence time, pathways of elimination by original and complementary methods described just below). The distribution in the vascular, interstitial and tissue space will be apprehended using cranial window devices.
- 4- Decrease the inflammatory effect and the polarization of macrophages through this treatment

Main results

So far we succeeded in synthesizing:

- DBCO-Peptide (19 mg purity 99%),
- DBCO-scramble peptide (scramble) (19 mg purity 93 %)
- NPs@DBCO- Peptide (165 mg)
- NPs@DBCO- scramble peptide (210 mg)

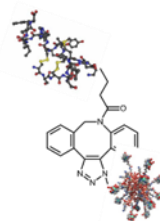


Figure 1: shamatization pf NPs@DBCO-peptide



Keywords : Ferulic acid, antioxidant, biocatalysis, polymer, building block

General context, scientific issues :

Ferulic acid is a phenolic acid widely present in plant biorefinery effluents, reaching concentrations as high as 8 g/kg of sugar beet pulp often used for animal feeding [1]. As potent antioxidant, this molecule is both interesting for the cosmetic and biomedical areas, where studies have shown its ability to be used as an anti-inflammatory and antitumoral agent. Nevertheless, ferulic acid presence in residual biorefinery effluents, as well as other phenolic acids, can greatly destabilize and alter bacterial communities in the soil [2]. In this context, the valorization of ferulic acid is necessary to avoid this pollution and to allow its application as an antioxidant agent.

Objectives and stakes :

The aim of this project is to use ferulic acid for the synthesis of building block molecules and polymers with antioxidant properties. These polymers can be used in the manufacture of active packaging to increase the shelf life of certain products [3]. For this purpose, it is necessary to change the chemical structure of the molecule to allow the polymerization and different routes of enzymatic reactions will be studied to obtain monomers derived from ferulic acid. Further, the most promising route will be optimized and used for the study of polymerization and polymers properties.

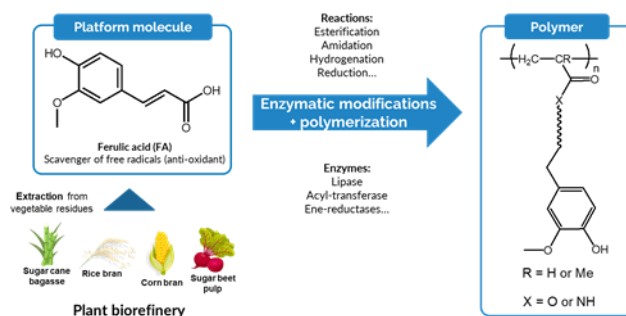
Methodology :

Several enzymatic routes will be studied to modify the ferulic acid molecule aiming to functionalize it for controlled radical polymerization, a type of polymerization with the ability to produce polymers with high molecular weight. These enzymes, from different families, will be used to derive ferulic acid into a diverse range of platform molecules that can be polymerized.

At first, the different pathways will be assessed to determine their feasibility. As each route is composed of a series of reactions performed by specific enzymes, every step will be individually studied. In the feasibility evaluation, small-scale experiments will be performed, to ensure that the desired products are formed during the reaction. Secondly, a kinetic study of the feasible pathways will be done, providing more information about the formation of the product and consumption of substrate during the reaction. This information will be used to guide the design of experiments, in which the different parameters of the reaction (temperature, molar ratio of substrates, enzyme load, duration) will be optimised for these reactions. Finally, a scale-up and process intensification will be done for the route with the highest productivity to produce enough monomer for the polymerization step. At this stage, the production of the polymer will allow the test of its mechanical performance and antioxidant property.

It must be stressed that, in the framework of this international LUE PhD thesis and thanks to the LUE DREAM program, two research stays of 3 months have been programmed at the TU Delft Department of biotechnology (The Netherlands) in order to get access to

Illustration : Ferulic acid valorization route





Main results

For each modification of the ferulic acid molecule, samples will be taken out before and after the reaction, which will be analyzed with HPLC coupled with a Photo Diode Array (PDA) and Mass Spectrometry (MS) for detection and determination of the products formed. The analysis will therefore provide information regarding the rate of conversion of the substrates, the selectivity of the enzyme towards the desired product, and the variation of each molecule concentration during the reaction.

In the feasibility step of the project, the expected result is the determination of the possible enzymes and reactions that can be used to modify the ferulic acid to produce monomers. At the second stage, it is anticipated that the studies will indicate the optimum condition for each modification step of ferulic acid that yields the highest productivity. The most promising pathway, with the highest final productivity, will be selected. In the final stage of the project, the expected results are the reactivity of the monomer produced towards controlled radical polymerization, as well as the mechanical and antioxidant properties of the produced polymers.

References :

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<p>2023</p> 	<p>Research subject: Combined experimental/numerical approach for the production and the characterization of new amino-acylases - Implementation in green N-acylation bioprocesses</p> <p>Laureline Gennesseaux (3rd year) Yann Guiavarc'h, Catherine Humeau BIOPROMO</p>	
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Keywords : enzymatic process, aminoacylase, N-acylation, enzyme structure-function relationships, production of recombinant enzymes, molecular modelling

General context, scientific issues :

Acylated derivatives of amino acids and peptides are interesting compounds for many industrial applications due to their emulsifying and foaming properties. The industrial scale production process is based on the Schotten Baumann's reaction, the main drawbacks of which are the use of acyl chlorides and organic solvents, a lack of selectivity and the production of toxic waste. The aminoacylases identified in *Streptomyces ambofaciens* supernatant specifically catalyze the N-acylation reaction in aqueous medium [1, 2, 3].

Illustration : 3D structure of SamAA obtained by ColabFold after adding metal ions



Objectives and stakes :

This project aims at developing a selective, efficient and eco-friendly bioprocess for the production of N-acylated derivatives of amino acids and peptides using enzymes of the aminoacylase type. This could constitute an alternative production pathway to the existing chemical production process.

Main results

The study began with the Sam_AA protein, which catalyzes the N-acylation reaction at the α position of amino acids. This enzyme is mainly produced as inclusion bodies in the *E. coli* system. Many operating parameters have been tested to solve this problem. SDS-PAGE analyzes showed no band of over-expression at the expected size of SamAA in the soluble fractions but these unpurified concentrated fractions were used for a synthesis of N- α -lauroyl-L-lysine at 45°C and pH8, in 48h which showed an apparent specific activity of 710mg/L of product/100mg of proteins/L of crude extract with cobalt in the culture medium. Similar work is in progress with the Sam_ELA enzyme catalyzing the N-acylation at the ϵ position of lysine. In parallel to this experimental approach, molecular modeling simulations were performed. The best 3D structure of SamAA and SamELA were shown to be that obtained by ColabFold [4]. Docking simulations are in progress to determine the key residues and interactions that are responsible for the selectivity of SamAA and SamELA towards the α and ϵ group of lysine respectively.

Methodology :

The study is organized according to two main issues:

- (1) intensifying the production and the purification of the two recombinant amino-acylases from *S. ambofaciens*.
- (2) studying the catalytic mechanism of these aminoacylases. Their structure will be predicted in silico using homology models. Enzyme-substrates binding modes will be determined with molecular docking simulations.

References :

- [1] Dettori et al., Micropor Mesopor Mat, 2018, 267:24-34
- [2] Dettori et al., Eng Life Sci, 2018, 18(8):589-599
- [3] Bourkaib et al., Enzyme Microb Tech, 2020, 137
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Keywords : Bioprocesses, Enzymes, Biosurfactants, Hempseed protein, Single Cell Protein

General context, scientific issues :

Biosurfactants are biomolecules mainly used in food, cosmetical and pharmaceutical industries. They can be synthesized through chemical/microbial/biochemical pathways in widescale. It is of very high interest the production of these molecules through processes which respect the human health and the natural environment¹. Among the different classes of biosurfactants, there is one of them which belongs to peptide/aminoacid derivatives and is formed by the grafting of fatty acids to peptides. To achieve this goal, a cooperation with Agricultural University of Athens (AUA) has been set up.

Hemp is cultivated worldwide for its components such as lipids, carbohydrates, proteins, minerals, phytonutrients. Hemp proteins have gathered huge interest for their various beneficial properties, so in order to acquire peptides and aminoacids from this plant, the extraction of proteins should be carried out and be followed by hydrolysis of them.

Microorganisms are able of producing high quantities of proteins² and fatty acids. Consequently, it could be considered as essential to valorize a low (even negative) cost industrial by-product, glycerol, as the source in which microorganisms can grow in order to biosynthesize proteins and fatty acids.

Objectives and stakes :

The objective is to produce amphiphilic compounds through "green" procedures in order to benefit by their multifunctional properties with no negative environmental impact. This can be achieved by the production of peptides by zero-cost plant by-products (such as hempseed meal) and through fermentations by microorganisms which produce Single Cell Protein. Moreover, the production of enzymes such as aminoacylases from *S. ambofaciens* is aimed in order to graft acyl groups³ on peptides/amino acids. These fatty acids can be produced from zygomycetes strains which accumulate large quantities of triacylglycerols (in collaboration with Agricultural University of Athens).

Methodology :

Initially, the crushing of hempseeds was done by oil cold-pressing machine so hempseed meal was obtained (kindly donated by a local farm). Firstly, the determination of the hempseed meal main components has to be performed. The grinding of hempseed meal (for better yield in extraction step) has been done by a blender and the protein extraction is envisaged to be catalyzed by enzymes (cell-wall degrading enzymes)⁴ in aqueous solution and a subsequent hydrolysis with different combinations of endo/exoproteases has to be performed in aqueous solution in order to achieve a high degree of hydrolysis and obtain (oligo)peptides/aminoacids which can be grafted with acyl groups and to synthesize biosurfactants.

Illustration : Schematic illustration of the methodology applied during this work





Main results

The partial defatting was done by oil cold-pressing procedure in the farm so greenish hempseed meal was obtained and no dehulling was carried out (increase of carbohydrates percentage in the meal). The average size of the (non-ground) hempseed meal particles is 808 μm . Before the extraction and the hydrolysis of hempseeds, the determination of the main hempseed components has been performed. The hempseed meal consists of 33 % proteins, 9.3 % lipids, 7.3 % ash, 10.4 % moisture and 41 % carbohydrates. This composition is similar to that already described in other studies⁴.

From the enzymatic extraction, cell-wall degrading enzymes such as cellulase, hemicellulase, xylanase, pectinase and ligninase will be used in different enzyme ratios and combinations. A percentage of 60-70% protein in the samples is expected to be obtained, with a protein extraction yield in the range of 15-35%. For the subsequent step of hempseeds hydrolysis, endo/exoproteases such as pepsin, pancreatin, papain, subtilisin, trypsin, chymotrypsin etc. will be chosen in different enzyme ratios and combinations as well, so different degrees of hydrolysis are expected (20-90%), knowing that the highest degrees of hydrolysis will be sought during these processes, to obtain short peptides or free

References :

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4. Pihlanto, A., Nurmi, M., Pap, N., Mäkinen, J. & Mäkinen, S. The Effect of Processing of Hempseed on Protein Recovery and Emulsification Properties. *Int. J. Food Sci.* 2021, 1–12 (2021).

	<p align="center">Research subject: CLIMBIN Project “Contrôle en Ligne pour la Maitrise de la Bioproduction Industrielle”</p> <p align="center">Sabrina HAMLA (Post doc) Emmanuel GUEDON, Bruno EBEL</p> <p align="center">BIOPROMO</p>	
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Keywords : Chinese Hamster Ovary cells (CHO), Process Analytical Technologies (PAT), molecular optical spectroscopies (MOS), multivariate data.

General context, scientific issues :

Monoclonal antibodies are experiencing a surge in the healthcare market. Regulatory agencies require continuous monitoring of animal cell culture processes for therapeutic purposes. In order to meet the needs of the biopharmaceutical industry, which seeks robust and reproducible bioprocesses with high productivity, the use of online quality control through process analytical technologies (PAT) is being developed. This approach has led to the emergence of a new generation of in situ and real-time monitoring tools “spectroscopic sensors” in order to control bio-processes.

Objectives and stakes :

The CLIMBIN project aims to develop an innovative analytical process control solution that addresses the optimization and automation challenges of cell culture systems in upstream (USP) and downstream (DSP) processes. This solution will enable biopharmaceutical industry to reduce production delays and costs, making therapeutic products more accessible to a larger number of patients. Among modern Process Analytical Technology (PAT) solutions, molecular optical spectroscopies (MOS) coupled with optical probes immersed in bioreactors are emerging as particularly promising for obtaining an overview of the biochemical state of the bioprocess. The choice of PAT-MOS in the CLIMBIN project focused on the development of UV-Visible multi-angle and Raman technologies, as they are not limited to a specific type of process or product and are applicable to all stages of production (USP - upstream process, DSP - downstream process, and QC - quality control)¹.

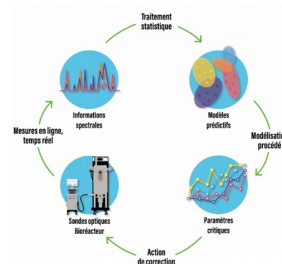
Methodology :

The first step in the study involves optimizing spectrophotometers acquisition parameters, such as integration time and number of scans. These spectrophotometers include UV-Visible multi-angle and Raman instruments used to monitor the kinetics (T0, T2, ..., T7) of Chinese Hamster Ovary (CHO) cell culture in Erlenmeyer flasks. The objective is to select the optimal parameters that result in a signal saturation rate ranging from 80% to 95%.

The second step, as illustrated in the figure, is to implement these probes (UV-Visible multi-angle and Raman) for real-time online measurements of a bioreactor (batch or feed batch). Spectra are acquired at periodic intervals of 1 hour. Throughout the culture process, reference data such as viable cell density (VCD) are obtained using the Vi-CELL XR™ automated cell counter from Beckman Coulter. Additionally, nutrient concentrations (glucose, glutamine), metabolites (lactate, NH₄⁺), enzymes (LDH), and antibodies (IgG) are measured using the Gallery™ spectral analyzer from Thermo Scientific.

Subsequently, spectral correction methods and exploratory data analysis techniques, such as principal component analysis (PCA), are employed to preprocess and clean the data. The acquired spectra from the UV-Visible and Raman spectrophotometers, along with the reference data, are then used to build quantitative predictive models. In this context, various regression methods, including linear models, such as partial least squares regression (PLSR) and nonlinear models, such as support vector regression (SVR), are considered and compared to establish a correlation between the spectral information and the quantitative reference values. The performance of the models is evaluated by comparing the results obtained from calibration, including root mean square error of cross-validation (RMSECV) and coefficient of determination (R²CV). As well as external validation, including root mean square error of prediction (RMSEP) and prediction coefficient of determination (R²)².

Illustration : : Real-time online measurement of critical parameters using optical probes involves several steps: 1- development of Quality by Design (QbD) and spectral acquisition. 2- statistical and spectral pre-processing. 3- prediction of critical parameters in constructed models. 4- Modeling and correction in the bioreactor



Main results

We expect several advantages and outcomes from the full PAT-MOS solution (instruments plus software) compared to current methods, including:



- By using the Quality by Design (QbD) approach, we will have a correlation between critical parameters (IgG, nutrients, metabolites) and their impact on the quality of the biopharmaceutical.
- Faster, more sensitive, and stable online measurements against perturbing factors, on any type of bioreactor, at all stages of bioproduction (USP, DSP, CQ).
- Robust Machine Learning models that adapt to all types of data, ready to use.

Integration of a large number of Critical Process Parameters (CPP) and Critical Quality Attributes (CQA) through the use of Artificial Intelligence (ML) and data fusion.

-Possibility of rapid decision-making by anticipating non-quality risks, with the prospect of automation of the control.

References :

- [1] D. A. Zavala-Ortiz et al., “Support Vector and Locally Weighted regressions to monitor monoclonal antibody glycosylation during CHO cell culture processes, an enhanced alternative to Partial Least Squares regression,” *Biochem. Eng. J.*, vol. 154, 2020, doi: 10.1016/j.bej.2019.107457.
- [2] S. Hamla et al., “A new alternative tool to analyse glycosylation in pharmaceutical proteins based on infrared spectroscopy combined with nonlinear support vector regression[†],” *Analyst*, vol. 147, no. 6, pp. 1086–1098, 2022, doi: 10.1039/d1an00697e

<p>2023</p> 	<p>Research subject: SELPHI Project : Development and implementation of an innovative methodology for in situ monitoring of cellular states during a culture process, without labelling and in real time, using holographic imaging</p> <p>Marine HERZOG (Study engineer)</p> <p>Emmanuel GUEDON, Bruno EBEL, Eric OLMOS</p> <p>BIOPROMO - MTinov</p>	
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Keywords : bioprocesses, holography, flow cytometry, animal cell culture, CHO, bioreactor

General context, scientific issues :

Biopharmaceuticals are of crucial importance in the therapeutic arsenal available to healthcare professionals and their production has become a global strategic issue both in term of competitiveness and sovereignty. For this purpose, the Selphi project aims to support the biosensor sector in order to promote new bioprocess monitoring solutions to enable French bioproduction players to improve their production capacities in this sector. Significant productivity improvements are expected with such monitoring tools and in particular for the monitoring of cell states during cell culture.

Objectives and stakes :

The overall objective of the SELPHI project is to develop and implement a new methodology for cell culture monitoring in almost real time, based on holography imaging. In collaboration with CEA-Leti, two major pharmaceutical companies (Sanofi and Servier) and a sensor device supplier (Iprasense), SELPHI aims to establish first the proof of concept of the early cell death detection in line, without cell labelling and in a non-invasive manner. Detection of cell physiology states and especially cell death are of crucial importance for biopharmaceutical production since it will have strong effects on productivities and qualities of bioproducts. Therefore, the monitoring of such bioprocesses could give access to qualitative and quantitative information on the culture in progress and will allow production enhancement.

Methodology :

In this project, experiments are based mainly on CHO cell culture processes. The objective is to obtain specific conditions of cell death induction. Cells analyses are performed using flow cytometry as the reference method to establish specific signals that will be compared with those obtained with holographic imaging. Several cell death induction will be tested in order to mimic conditions that are encountered in industrial processes (chemical, O₂ deprivation, nutrients limitation...).

Illustration : Holographic monitoring of CHO cell culture process





Main results

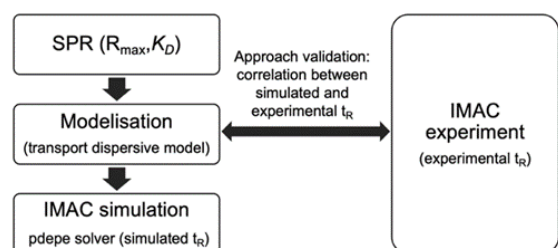
In collaboration with partners (see objectives and stakes), a relationship between very early apoptosis cell characteristics and holographic signals will be established. Then, an in situ holographic sensor that could be implemented directly in the bioreactor will be developed, allowing direct control of the process.

References :

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- [2] Hervé L. et al "Alternation of inverse problem approach and deep learning for lens free microscopy image reconstruction", *Nature Scientific report*, (2020) 10:20207 | <https://doi.org/10.1038/s41598-020-76411-9>
- [3] Mandenius, Carl-Fredrik. "Measurement Technologies for Upstream and Downstream Bioprocessing." *Processes* 9.1 (2021): 143.



<p>2023</p> 	<p>Research subject: Metal-chelating peptides and chromatography: from peptides separation to metals separation</p> <p>Rachel Irankunda (3rd year)</p> <p>Laetitia Canabady-Rochelle, Laurence Muhr</p> <p>BIOPROMO, PERSEVAL</p>	
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Keywords : Metal-Chelating Peptides (MCPs), Immobilized Metal ion Affinity Chromatography (IMAC), Surface Plasmon Resonance (SPR), chromatography modelling and simulation, separation, lipid oxidation.

<p>General context, scientific issues :</p> <p>MCPs, present in mixture of peptides (hydrolysates), are able to complex metal ions, which confers them various applications in nutrition and cosmetic [1]. Yet, MCPs separation is challenging due to their low concentration in hydrolysates. To date, MCPs are discovered by an empirical approach and other alternatives to separate MCPs from the peptide mixture should be found.</p>	<p>Illustration : Approach for simulating peptide separation in IMAC [5]</p> 
<p>Objectives and stakes :</p> <p>This thesis aims (i) to predict the separation of MCPs in IMAC using SPR peptide affinity data and chromatographic modeling by the dispersive transport model, considering the SPR-IMAC analogy as both methods are based on peptide-metal interaction. The other objective (ii) is to study the application of peptides in the food field to inhibit lipid oxidation in oil-water emulsions.</p>	<p>Main results</p> <p>The SPR results showed that some peptides had high affinity constants (high K_A, low K_D), meaning a good affinity for Ni^{2+}. On the other hand, these same peptides studied in IMAC showed that some peptides were retained longer in the column (high retention time), which means that they have a good affinity for Ni^{2+}. The IMAC and SPR results proved experimentally the correlation between these two methods, as the majority of peptides with good affinity in SPR are also well retained in IMAC. Currently, the chromatography modeling is under optimization to allow the simulation of the retention times of peptides from the SPR input data.</p> <p>Besides, peptides that showed an ability to chelate Ni^{2+} - and thus probably Fe^{2+} as intermediate acid ion as well - were investigated for their ability to inhibit lipid oxidation in oil-in-water emulsion, in collaboration with DTU Denmark (DrEAM 6 mobility). The peptides with good affinity to Ni^{2+} - according to SPR - chelated Fe^{2+} well known to catalyze lipid oxidation. Thus, the formation of volatile compounds responsible for bad odors and deterioration of emulsion products (e.g., mayonnaise, salad dressings) upon oxidation was decreased. Therefore, these peptides could be used in industrial products to prevent lipid oxidation.</p>
<p>Methodology :</p> <p>Peptide sequences to investigate were obtained from pea proteins theoretical hydrolysis. These synthetic peptides were studied in SPR using a Ni^{2+}-NTA sensor chip, a biosensor method for screening MCPs in hydrolysates [2]. From SPR, peptide sorption isotherms were obtained and thus their binding affinity parameters (K_A, q_{max}) calculated. These former parameters served as input data for peptide retention time (t_R) simulation in IMAC. A transport dispersive model [3] that describes the transfer phenomena in the chromatographic column was used.</p> <p>On the other side, the same peptides were investigated in IMAC using a HiFloQ-Ni^{2+}-NTA column in order to make correlation between the experimental t_R and the simulated t_R to validate the approach, the proof of concept was already published [4].</p>	<p>References :</p> <p>[1] Guo L. et al., Trends Food Sci. Tech. 2014, 37:92–105.</p> <p>[2] Canabady-Rochelle L. et al., Food Chem. 2018, 239:478–485.</p> <p>[3] Guiochon G. et al., Trends Food Sci. Tech. 2006, ISBN: 978-0-12-370537-2</p> <p>[4] Muhr L. et al., J. Sep. Sci. 2020, 43:2031–2041.</p> <p>[5] Irankunda et al., Separations. 2022, 9(11), 370.</p>

Acknowledgements :

Authors acknowledge financial support from MESR grant, ANR JCJC MELISSA, ICEEL INTRA 2019, DrEAM 6 (UL).

<p>2023</p> 	<p>Research subject: Development and validation of a metabolic model of a hydrogen-producing bacterial consortium</p> <p>Xavier Marbehan (3rd year) Stéphane Delaunay, Frantz Fournier</p> <p>BIOPROMO</p>	
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Keywords : Metabolic modeling, Flux Balance Analysis (FBA), Biohydrogen, Bacterial interaction

General context, scientific issues :

The use of hydrogen as an energy carrier is a relevant alternative to fossil fuels, provided that its production is clean and does not require fossil resources. One promising approach would be to produce bio-H₂ using microbial organisms. Among interesting microbial candidates, a consortium has been selected in the framework of the ANR project EPIC-H₂. This consortium is composed of two micro-organisms: *Desulfovibrio vulgaris* (Dvu) and *Clostridium acetobutylicum* (Cac) which seem act in symbiosis for the production of biohydrogen. Indeed, the amount of produced hydrogen by the consortium is higher than the sum of hydrogen produced by the two micro-organisms independently [1].

Objectives and stakes :

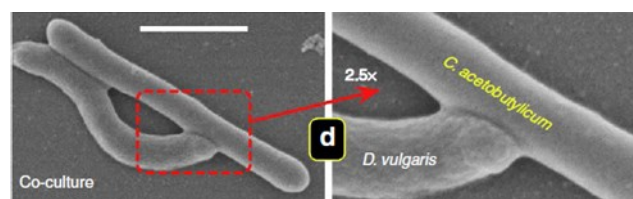
A transfer of metabolites between the two bacterial partners of the consortium is suspected to be responsible for the biohydrogen overproduction. To identify the exchanged metabolites, it is planned to model the global metabolism of the bacterial consortium. This modeling study requires several steps. First the metabolic modeling for each organism composing the consortium has to be performed. Then, from these individual models, a community model for the consortium will be constructed. Later, this model will be used to determine the impact of spatial and temporal variations of the consortium environment on the metabolism and on the biohydrogen production.

Methodology :

The construction of a numerical model was performed from biochemical reactions listed in databases, as well as in the scientific literature. Some models also existed in the literature but have to be adapted to our case study.

To solve the models, the simulation tool CobraToolbox (Matlab software) has been used. Using an adequate solver, the respective metabolic flux of each reaction contained in the models have been calculated according to the "flux balance analysis (FBA)" method. To solve the consortium model, an original multi-objectives numerical tool named Xcom was then developed [2].

Illustration : Contact between *D. vulgaris* and *C. acetobutylicum* [3].



Main results



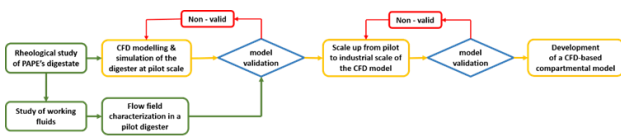
A simulation of the consortium model with constraints recreating the experimental environment was performed. These constraints were imposed fluxes of glucose consumption by Cac and of a carbon source by Dvu, this one provided exclusively by Cac. The other constraint was the possibility, for both bacteria, to exchange, in the physical bridge (illustration), all their common intracellular metabolites. The fluxes found for the biomass synthesis of each organism and the global hydrogen production were compared with and without exchange between cac and dvu.



It appeared that the metabolite exchange led to an overproduction of hydrogen. This confirmed the experimental results previously obtained by Benomar et al. (2015) [3]. An electron exchange between cac and dvu is suspected to be responsible for this increased hydrogen production.

However, the extent of this electron exchange and its precise mechanism remain to be fully elucidated. Several hypotheses are being examined, including the possibility of direct interspecies electron transfer (DIET) via electrically conductive pili, or nanowires, as well as indirect electron transfer via secreted redox-active metabolites.

References :

- [1] Barca et al. « Fermentative Hydrogen Production in an Up-Flow Anaerobic Biofilm Reactor Inoculated with a Co-Culture of *Clostridium Acetobutylicum* and *Desulfovibrio Vulgaris* ». *Bioresource Technology* 221 (décembre 2016): 526-533. <https://doi.org/10.1016/j.biortech.2016.09.072>.
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<p>2023</p> 	<p>Research subject: Modelling of the hydrodynamics of an agricultural digester</p> <p>Liliane Megue Kamkeng (3rd year) Éric OLMOS, Benjamin LE-CREURER BIOPROMO, Air Liquide</p>	
<p>Keywords : agricultural digester, hydrodynamics, rheology, scale-up, CFD modelling</p>		
<p>General context, scientific issues :</p> <p>Inadequate mixing in digesters can significantly contribute to the failure of biogas production [1,2]. Thereby, the establishment of optimal mixing conditions (impeller design, agitation mode and frequency) would ensure a good homogeneity of the reaction medium and thus an intensification of biogas production with a minimal power consumption for mixing. To achieve this, it is needed to better describe the fluid flow that occurs within the digester.</p>	<p>Illustration : Graphical illustration of the research methodology</p> 	
<p>Objectives and stakes :</p> <p>This thesis aims to develop a hydrodynamic model of an industrial digester. More specifically, this research intends to optimize the agitation of the industrial digester from Pot au Pin Énergie (PAPE) in Cestas-France, to limit the energy consumption and avoid sedimentation. The PAPE's digester is a continuous stirred tank reactor (CSTR) of roughly 2000 m3 volume and fed with a mixture of corn silage and rye.</p>	<p>Main results</p> <p>Rheological measurements showed that the PAPE's digestate exhibits a non-Newtonian shear thinning with yield stress behavior described by the Herschel-Bulkley model. This result was used to design a pilot digester with geometric, hydrodynamics and mixing performance similar to the industrial digester. The scale-down approach was validated by experiments (Particle Image Velocimetry measurements) and CFD simulations. CFD models at both scales are able to capture the main features of the flow. The models also allow the prediction of the agitation power consumption with an average error of 4 %. A hydrodynamic compartmental model of the industrial digester is being developed based on the CFD model. This compartmental model can be coupled with a biokinetic model to consider the hydrodynamics involved in the anaerobic digestion process during the simulation of the anaerobic digester.</p>	
<p>Methodology :</p> <p>First, experimental work was carried out to characterize the rheology of PAPE's digestate and the flow field in the digester at a reduced scale. CFD modelling of the pilot digester was then performed, followed by model validation. Finally, the CFD model was applied at the industrial scale based on some scale-up criteria to predict the hydrodynamics in the PAPE digester.</p>	<p>References :</p> <p>[1] Karim et al., Water Research 2004, 38(17):3659–3670. [2] Lebranchu et al., Bioresource Technology 2017, 245:1139–1147</p>	

<p>2023</p> 	<p>Research subject: Synthesis of photosensitizers to target, detect and destroy peritoneal carcinomatosis by photodynamic therapy.</p> <p>Morgane Moinard (2nd year)</p> <p>Céline Frochot, Nadira Delhem</p> <p>BIOPROMO, OncoThai (Lille)</p>	
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Keywords : photodynamic therapy, photosensitizers, folic acid, ovarian cancer, peritoneal carcinomatosis

General context, scientific issues :

Because of a lack of symptoms, ovarian cancer is often diagnosed at an advanced stage of the disease. Despite a conventional treatment combining platinum-based chemotherapy to maximal cytoreduction surgery, about 60% of women relapse¹. This high recurrence rate is mainly due to the presence of microscopic peritoneal carcinomatosis residues, not visible to the naked eye of the surgeon, which were not removed after surgery. In order to increase the life expectancy of diseased women, our research project aimed to specifically target these microscopic tumoral residues.

Our main strategy is the active targeting of the α isoform of folic acid receptor (FR α), by using photodynamic therapy (PDT). In fact, this receptor is overexpressed by various cancer cells, including those of ovarian origin². Furthermore, the main advantage by targeting FR α is that this latter is only slightly expressed by healthy cells and tissues, allowing a specific target to ovarian cancer cells and metastasis. In this context, various photosensitizers (PS) coupled to folic acid molecule have been previously synthesized by our research group. One of them was the object of one patent. But some stability issues were observed with the folic acid molecule³. In fact, some degradation products were observed upon illumination. Therefore, our main objective is to design folic acid analogue which could circumvent this stability problem. Indeed, based on molecular docking studies, some folic acid analogues with a potential affinity to folic acid receptor should be developed.

Objectives and stakes :

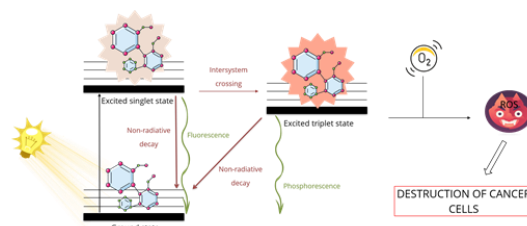
Our goal is to synthesize these new folic acid analogues which would potentially target the FR α receptor and to combine them via a PEG spacer with a PS, for PDT treatment of peritoneal carcinomatosis. Three main parts composed our project:

- Synthesis of folic acid analogues followed by coupling with a PS.
- Investigation of photophysical properties of the newly synthesized PS.
- Biological investigation of the PS in vitro and in vivo.

Methodology :

- Organic synthesis methodology and purification by HPLC or column chromatography.
- Characterization of compounds by HPLC, MS, RMN 1H and 13C.
- Photophysical characterization: UV-visible absorption, fluorescence emission, singlet oxygen and ROS production.
- Photostability studies.
- Biological tests

Illustration : Photodynamic therapy principle.



Main results

We have coupled folic acid analogues to a PS via a PEG spacer, to obtain a targeted PDT effect towards ovarian cancer cells. We synthesized, purified, and characterized a first new photosensitizer (PSAAF1), resulting from a coupling between a folic acid analogue and pyropheophorbide via a PEG spacer. The folic acid analogue is the result of 10 steps with an overall yield of 13%. Photophysical properties (quantum yields and lifetimes of fluorescence and singlet oxygen, photobleaching) of PSAAF1 was investigated in EtOH. We found a fluorescence quantum yield of 0.26 and a singlet oxygen quantum yield of 0.41. Regarding biological studies, no dark toxicity was observed in vitro for a concentration up to 9 μ M. Phototoxicity in three cancer cell lines (the SKOV3, OVCAR3 and HT1080) were performed. In each cancer cell lines, after illumination with a 672 nm laser for 5 minutes, cellular viability was closed to 0% at concentration of 1.8 μ M and 4.5 μ M. 100% of cells were killed at a concentration of 9 μ M.

Perspectives

PSAAF1 will be coupled to others PS in order to study its stability in function of the one with which it is coupled.

A second folic acid analogue is currently under synthesis. This second analogue will also be coupled to various PS via PEG spacer.

References :

- [1] Truc A. et al., Chem. Eng. J. 2020, 45:205-210.
- [1] Al Rawahi T. et al., Cochrane Database of Systematic Reviews
- [2] Parker N. et al., Analytical Biochemistry, 2005, 338, 284–293.
- [3] Gazzali M. et al., European Journal of Pharmaceutical Sciences, 2016, 93, 419–430.
- [4] Moinard M. et al., Pharmaceuticals, 2022.



Keywords : Mesenchymal Stem cells, bioprocess, flow cytometry, control quality (CQ), bioreactor

General context, scientific issues :

The production of biomedicines has now become a major strategic target for France and worldwide, specifically through the increasing use of recombinant proteins and innovative therapies, including cell and gene therapies.

The LRGP is a partner of the OPTI-STEM2 project, which aims to optimize the production of mesenchymal stem cells (MSC) to democratize access and thus allow the diversification of therapeutic applications of this type of cells and their derivatives.

When preparing MSC for clinical uses, many sources of variation can impact the quality and bioactivity of the cells, such as the donor (genetics, gender, age), the MSC source, the cell expansion capacity (depending on the culture conditions, number of passages, the cell surface changes etc.) [1]

Objectives and stakes :

In this project, some of the objectives will be to carry out the quality controls of cells produced (1) in 2D in flasks and (2) in 3D on microcarriers suspended in a controlled and stirred bioreactor. For that, the phenotype of cells will be assessed throughout the culture to check the cellular physiology (surface markers, viability, differentiation stage, size) and understand the impact of the methods of culture on the state of the MSCs. Ultimately, the goal will be to develop a bioprocess where stem cells will be obtained in large quantities in GMP-like conditions to allow an easier transition of the methods into clinical applications.

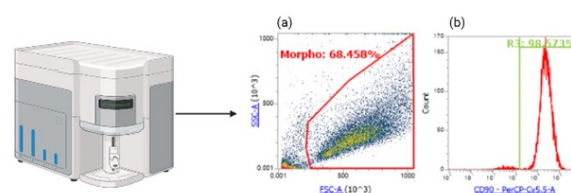
Methodology :

To control the quality and strain of the cells produced, flow cytometry tests will be performed to monitor and compare cell phenotype between 2D and 3D cultures. The target cells will be labeled with fluorochrome-coupled antibodies, allowing us to sort them according to the level of expression of various markers.

In 2006, MSCs were defined by the ISCT as adherent cells with a spindle-shaped morphology and with the ability to differentiate into osteoblasts, adipocytes or chondroblasts. They are also defined by the expression of characteristic mesenchymal markers such as CD73, CD105 or CD90. Moreover, it is important during the culture phase to follow the evolution of specific markers of endothelial (CD34), immune (CD14) and hematopoietic (CD45) cells to confirm the non-differentiation of the produced MSCs. [2]

Thus, the first step will be to develop specific protocols to MSCs according to their profile. Each cell type being morphologically different and not expressing their same markers, it will be necessary to adapt each protocol to make them as adjusted as possible.

Illustration : Cell sorting with flow cytometry by (a) their size (FSC Forward Scatter) and their granularity (SSC Side Scatter) and according to (b) the expression of a surface marker, detected by an antibody coupled to a fluorochrome (here CD90-PerCep-Cy5.5).



Main results



Currently, the culture of MSC in 2D and 3D on microcarriers in spinners is controlled, and it results in a high cell density and a good viability of cells. In the coming months, tests in stirred bioreactors will be carried out, with a phenotypic assessment of the cells by flow cytometry throughout the culture. Preliminary tests have been performed to target the cultured MSCs according to their morphology (fig. 1a) and test the antibodies targeting the biomarkers of interest (fig. 1b).

For the continuation of the project, it will be interesting to check (1) the bioactivity of the cells produced by testing their immune-suppressive capacity against immune cells or their ability to migrate, and (2) to study by RT-qPCR the gene expression of adipocyte, osteogenic and chondrogenic transcription factors in order to determine their differentiation stage.

Finally, different culture media will be preselected by one of the project's partners (CellEasy) and tested under our growing conditions. The main objective is to cultivate MSCs in a medium without serum or platelet lysate to allow the translation of the method safely for human use (absence of xenogenetic product). These experiments will require an assessment of MSCs proliferation, viability and quality control testing.

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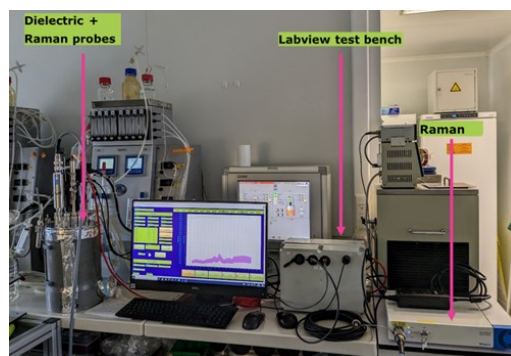
<p>2023</p> 	<p>Research subject : Innovative coupling of sensors integrated in bioprocesses for real-time monitoring of the physiological and metabolic status of eukaryotic cells</p> <p>SCHINI Adèle (2nd year)</p> <p>Emmanuel GUEDON, Bruno EBEL</p> <p>BIOPROMO</p>	
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Keywords : bioprocesses, spectroscopies, in situ sensors, animal cell culture, CHO, bioreactor, optimization

General context, scientific issues :

The PAT (Process Analytical Technology) approach consists in developing online monitoring methodologies for production processes to ensure their real-time control. However, apart from the classical probes (pH, temperature, O₂ concentration), the bioreactors of animal cell cultures remain very little instrumented. To overcome this lack, spectroscopic tools coupled to sterilizable fiber optical probes are beginning to be evaluated.

Illustration : Example of a test bench performed during a cell culture to monitor cell growth



Objectives and stakes :

The overall objective of this thesis work is to lay the first building blocks for the combination of sensors used in bioprocesses. Thus, the monitoring of industrial processes could move from "Process Control" to "Quality Attribute" which gives access to qualitative and quantitative information on the culture in progress. Obtaining in situ information related to cell metabolism and reaction kinetics will allow production enhancement and process control.

Main results



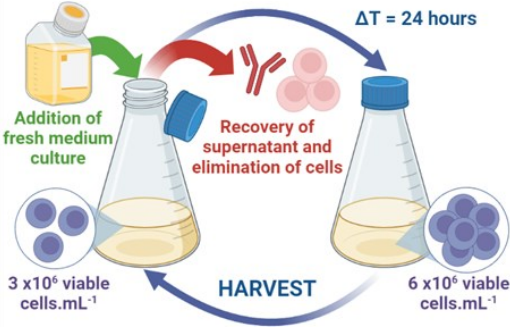
Several cell culture processes have been performed over this year. They allow to determine calibration models in order to monitor parameters that can be used to establish a feeding strategy of cell culture processes. In particular, such strategy will give the user access to the control of qualitative and quantitative information about the current cell culture process.



Methodology :

The modeling of the raw spectroscopy measurements is the first milestone of this thesis. The conversion of these data into numerical values related to cells in culture will be optimized and adjusted as much as possible. The objective is to obtain in real time a global view of the physiological state of the cells in culture. For the qualitative aspect, a coupling of spectroscopies will be realized. An innovative model giving access to the physiological aspect of cells and their metabolic state will be built. Several cell culture runs have to be performed to assess the accuracy of the modeling approaches.

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<p>2023</p> 	<p>Research subject: Bioproduction project: Innovative Technology Solution for Micro/Mili Electrophoresis (IT'SME)</p> <p>Schneider Samuel, Study engineer</p> <p>BIOPROMO</p>	
<p>Keywords : Chinese Ovary Hamster (CHO), cell culture, bioreactor, harvest, bioprocess, monoclonal antibody, IgG, purification, microelectrophoresis.</p>		
<p>General context, scientific issues :</p> <p>The use of immunoglobulin G (IgG) has become a preferred strategy for combating various diseases related to oncology, hematology and immunology [1]. In the context of industrial IgG production, the process can be divided into two main distinct steps: upstream processes (USP) encompassing the cell culture steps in bioreactors, and downstream processes (DSP) including purification of the drug substance. Currently, the majority of purification steps are performed by liquid chromatography. Although effective in purifying complex mixtures, chromatography suffers from major practical, economic and environmental drawbacks.</p>	<p>Illustration : Description of the harvest culture in Erlenmeyer flask</p> 	
<p>Objectives and stakes :</p> <p>The objective is to couple a new biomolecule purification tool, based on the principle of free-flow microelectrophoresis (μFFE), to a bioreactor culture of CHO cells. This approach will allow the purification of IgG without the use of conventional chromatographic methods. Thus, the success of such a project will constitute a significant advance in the design of modular, automated and flexible plants for the production of biomedicines.</p>	<p>Main results</p> <p>This experiment addresses the previously mentioned primary issue. Although CHO cells can be cultured for several successive passages, their IgG productivity may decrease over time due to genetic mutations or epigenetic changes [2]. In this study, the CHO M250 cell line, which produces anti-Rh D IgG, was cultivated using the harvest mode in ventilated Erlenmeyer flasks for 41 days. Throughout this kinetic process, cell viability values were maintained between 3 and 6 x 10⁶ cells.mL⁻¹. The cells were capable of doubling their population after each dilution. Additionally, viability percentages were maintained above 90% throughout the culture. These results indicate good overall cell viability, making the obtained results applicable. Moreover, extracellular IgG concentrations were measured to evaluate cell productivity. Normalized to the number of cells, this production remained constant for 24 days at concentrations on the order of 3x10⁻¹¹ grams/cell. Taken together, these findings appear promising for long-term IgG production in a continuously per-</p>	
<p>Methodology :</p> <p>The project includes three steps: ❶ Determination of maximum culture times for sufficient maintenance of cell growth, viability and extracellular IgG production. ❷ Implantation of CHO cell cultures in a continuous perfused bioreactor and optimisation of the process to maximise the specific IgG productivity of the cells. ❸ Coupling of the bioreactor with one or more μFFE to obtain the desired purity and comparison of the results with those obtained by conventional HPLC.</p>	<p>References :</p> <p>[1] Carrara, S.C., Ulitzka, M., Grzeschik, J., Kornmann, H., Hock, B., and Kolmar, H. (2021). From cell line development to the formulated drug product: The art of manufacturing therapeutic monoclonal antibodies. <i>International Journal of Pharmaceutics</i> 594, 120164. 10.1016/j.ijpharm.2020.120164.</p> <p>[2] Beckmann, T.F., Krämer, O., Klausning, S., Heinrich, C., Thüte, T., Büntemeyer, H., Hoffrogge, R., and Noll, T. (2012). Effects of high passage cultivation on CHO cells: a global analysis. <i>Appl Microbiol Biotechnol</i> 94, 659–671. 10.1007/s00253-011-3806-1.</p>	

<p>2023</p> 	<p>Research subject: Optimization of human adipose derived stem cells culture in stirred tank reactor in order to scale-up to 50 L.</p> <p>Bastien Thauvin (2nd year)</p> <p>Latifa Chebil (LRGP), Eric Olmos (LRGP), Julien Branchu (EVerZom), Camille Simon (EVerZom)</p> <p>BIOPROMO, EVerZom (Paris)</p>	
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Keywords : cell culture, microcarrier, bead-to-bead transfer, mesenchymal stem cells, bioreactor

General context, scientific issues :

Extracellular vesicles (EVs) produced by mesenchymal stem cells (MSC) are promising cell-free therapies to repair damaged tissues in regenerative medicine or for their immunomodulatory properties [1]. However, lack of large-scale GMP compatible EVs production processes limits clinical translation. EVs production yield can be improved by mechanical stress induced by turbulence[2] but a large number of cells is still required.

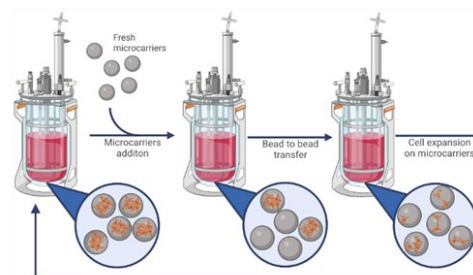
Objectives and stakes :

The aim of this PhD project is to design a cell culture process compatible with regulatory standards to produce the large amount of MSCs required to support EVs therapies development. MSC are anchorage-dependent and need specific surface area for their expansion. Conventional 2-Dimensional systems are time consuming and allow insufficient control of cell culture parameters. Development of 3D culture systems on microcarriers tends to give interesting solutions to address these issues [3]. Moreover, it was previously shown that MSCs can migrate from confluent microcarrier to new empty ones which is called bead to bead transfer (Btb) ; adding new microcarriers thus increase specific area for cell growth without using enzyme for cell detachment and cell passage. One of the main objectives of this PhD is to optimize BtB protocol to reduce global costs of the EV production.

Methodology :

Human adipose derived stem cells (ADSCs) were cultivated in a 1,2 L stirred tank reactor (STR) with and without microcarriers addition. Btb is carried out by withdrawing half of the culture volume, followed by adjustment through the addition of fresh medium and microcarriers at an identical concentration. Transient intermittent agitation [4] was applied after each feed to favor cell migration. Metabolites are monitored by an automate Gallery multiparametric analyser and cell distribution on microcarriers are measured by nuclei staining with microscopy completed by an in-situ permittivity measurement. At the end of each culture, EVs production is carried out by stimulating the cells with turbulence. The suspension is then clarified, and the vesicles are characterized using Nanoparticle Tracking Analysis.

Illustration : Scale-up of ADSC culture process using bead to bead transfer to provide more surface available for cell expansion


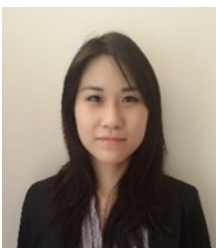


Main results

Several successive microcarrier additions have been achieved during cell expansion and Btb sensibly increased final theoretical attached cells number within a factor 9 in comparison with control cultures and also allowed to lengthen the expansion phase. Btb also reduced the number of densely and overloaded microcarriers that limit cell growth inhibition and delayed the formation of unwanted aggregates. The duration of intermittent agitation cycles was improved to favor cell migration with more than 95 % of microcarriers occupied by at least one cell after each addition. The number of cells per microcarrier was also precisely defined at the fresh microcarrier feed to limit large aggregates and to conserve minimal cell density to continue cell growth. As a conclusion, this scale-up method is promising to obtain large number of cells required for the development of EV based therapies. For the future, it is planned to validate the process in a GMP-like 10 L bioreactor. Finally, characterization of cells and EVs will be carried out to ensure conservation of therapeutics properties throughout the production process

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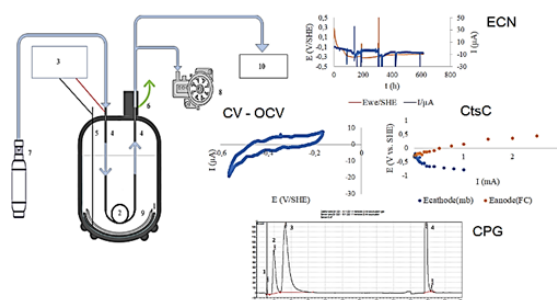
<p>2023</p> 	<p>Research subject: Electrochemical investigation of Microbial MEC for hydrogen production process</p> <p>Delphine Truong (4th year)</p> <p>Emmanuel Guedon, Mathieu Etienne</p> <p>BIOPROMO, LCPME</p>	
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Keywords : MEC, dark fermentation, hydrogen, electroactive bacteria, biofilms, organic waste

General context, scientific issues :

In the context of the energy crisis which depends on fossil fuels, hydrogen could be also as a powerful clean energy vector but are mainly produced through petrochemistry process. Bioproduction of hydrogen using dark fermentation (DF) and Microbial Electrolysis Cells (MEC) is an alternative.

Illustration : Experimental approach for bio-H₂ production



Objectives and stakes :

The aim of the work is to combine DF and MEC into the same bioreactor to produce H₂ without external energy supply, using a constituted microbial ecosystem taken from a biomethanizer (experimental farm, la Bouzule, Université de Lorraine). The objectives are the production of current and a microbial specialization at both electrodes, in order to improve H₂ production.

Main results

Electrodes were connected to a potentiostat in order to measure the system potential and current naturally reached in its equilibrium state.

The system potential reached -321 mV vs. SHE with a current density of 5,21 mA/m². The potential seems to be the maximum that can be reached by bacteria and it is close to the redox potential of NADH/NADH⁺ which is one of co-factor couples used for biohydrogen production.

The potential of each electrode was first measured by disconnecting the system. Then, regarding of this potential, the system is reconnected, and a range of potential, containing the system potential, was applied. The responded current is measured. This allows to see different oxidation and reduction reactions on each electrode.

The O₂ contamination was controlled and methanogens microorganism were inhibited. H₂ production was observed in gas chromatography which means that its production could be reach at the system potential.

To determine the limit of the system, a range of current was applied on each electrode for 6h and the corresponding potential was measured.

The carbon felt used as anode seems to have a sufficient surface to support electron flow for the H₂ production. Thus, a first limit between biotic and electrolysis H₂ production has been showed at the cathode (close to -515 mV vs. SHE).



Methodology :

A tubular silicone-carbon membrane is used either as a cathode and also for gases extraction. Anode is made of carbon felt. Gas extraction from the medium is carried out by a vacuum of 2.5 bar through the tubular membrane. Electrodes are connected to a potentiostat to measure potential and current during the time. Voltametry tests are also made using the same potentiostat.

A 5L scale bioreactor, is used as a single reaction chamber. Organic material is taken from a biomethanizer and used with or without treatment (to inhibit methanogenic bacteria). Gas produced were analysed using a gas chromatography.

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<p>2023</p> 	<p>Research subject: Coupling of anaerobic dark fermentation and biomethanation for biomethane production.</p> <p>Ludovic Vauthier (1st year)</p> <p>Stéphane Delaunay, Emmanuel Guedon, Emmanuel Rondags, Céline Loubière, Xavier Framboisier</p> <p>BIOPROMO</p>	
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Keywords : bioenergy, hydrogen, methane, microbial process, fermentation, bioconversion

General context, scientific issues :

The degradation of organic matter through anaerobic digestion results in a biogas composed by approximately 55% of CH₄ and 40% of CO₂, which is not energetic enough to be directly injected into the natural gas network. The aim of the present research is to convert the CO₂ into CH₄ to increase the methane content of the biogas.

Objectives and stakes :

To improve the CH₄ yield, 2 complementary biological processes are used. The first process, called “dark fermentation” (because it does not require light energy) is performed by several bacterial species, especially those of the genus *Clostridium*. They can convert hexoses into other metabolites along with an interesting by-product: dihydrogen. This H₂ will then be transferred to a microbial consortium (second process), for the bioconversion of CO₂ and H₂ into CH₄.

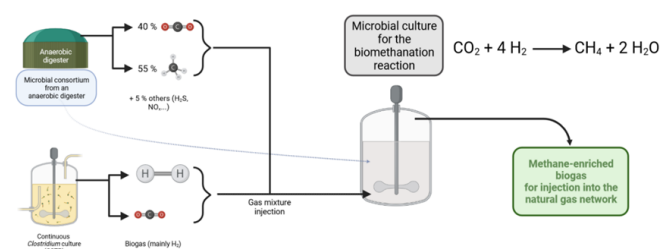
Methodology :

Firstly, several batch cultures will be performed in a 1,5L-bioreactor with different *Clostridia* species to select the strain with the most interesting performances in terms of growth and biogas productivity. Cultures will then be carried out in continuous mode with the selected strain to find the best conditions for biohydrogen production (pH, dilution rate, substrate concentration) using a Design of Experiments approach. Different types of substrates could also be tested.

Secondly, the produced biogas will be transferred to another fermenter containing the microbial consortium from a digester. It will be necessary to determine the efficiency of the biohydrogen transfer throughout this process, as it could possibly be a technical bottleneck, where solutions need to be found to improve CO₂ conversion. It could also be interesting to evaluate the effect of the biogas composition on the microbial consortium physiology. The biogas may be purified prior to the transfer.

Finally, the whole coupled process could be modelled from a kinetic or metabolic point of view to identify the key parameters for scaling up the developed process.

Illustration : diagram of the two coupled processes





Main results

The experiments carried out so far mainly consisted of finding the best medium composition for discontinuous cultures and evaluating the performances of 5 *Clostridia* strains. A *Clostridium acetobutylicum* strain showed the best performance in terms of biogas productivity (almost 800 mL of biogas per hour, with an initial glucose concentration of 20 g/L). A *Clostridium tyrobutyricum* strain was able to produce the highest amount of gas at the end of the culture (9.7 L under the same culture conditions). 3 other strains need to be cultured to draw conclusions and to pursue experiments with continuous cultures. The amount of metabolites produced during the cultures will be evaluated by HPLC to determine the hydrogen rate in the biogas and to calculate several kinetics parameters. The strain with the most interesting parameters will be selected to start continuous cultures before the end of the year.

References :

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	<p>Research subject: Optimization of the production of Mesenchymal Stem Cells (MSC) in stirred tank bioreactors for therapeutic purposes</p> <p>Astrid Zayana (study engineer), Isabelle Chevalot, Celine Loubière, Jessica Schiavi BIOPROMO, CellEasy</p>	
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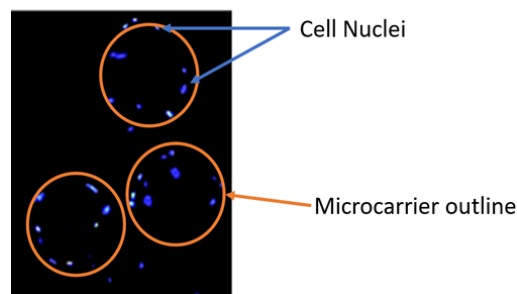
Keywords : Stem cells, bioprocess, optimization, scale-up, bioreactor

General context, scientific issues :

The development of Innovative Therapy Medicines (MTIs) based on mesenchymal stem cells (MSCs) is faced with excessive production costs which limit their accessibility to patients (Olsen et al. 2018) and discouraging reimbursement agencies in a context of budgetary constraints in many countries.

To achieve this goal, MSCs are cultivated on microcarriers placed in stirred bioreactors to enhance the production intensity and better control over operational conditions, thereby impacting product quality. Nevertheless, scaling up the process remains a challenge due to clinical production constraints and the fragile nature of the cells.

Illustration : Observation of Cell Nuclei-Stained Blue Under UV Light with DAPI.



Objectives and stakes :

The objective of the project is to develop a robust and controlled bioprocess to produce large quantities of MSCs from adipose tissue by seeding them microcarriers and cultivating them within an agitated and instrumented bioreactor. The main challenge in MSC production lies in the scaling-up of the process. To overcome this, we intend to adapt the batch culture method in T-flask to a fed-batch or continuous mode in bioreactor. This innovative approach will enable us to gradually expand the culture surface as the cells proliferate. Furthermore, this approach has the potential to significantly reduce the manufacturing price, possibly by a factor of 100, and achieve a production capacity exceeding 100,000 doses per year. Developing a cell culture process on microcarriers within a bioreactor requires the determination of several critical parameters. For example, several researchers are working on the selection of appropriate microcarriers, the optimization of the composition of the culture medium, and the determination of the optimal agitation speed. These parameters can be systematically optimized using a design of experiments approach and subsequently improving the scale-up to larger production volumes while ensuring compliance with good manufacturing practices.

Main results

The first screening step led to the pre-selection of 5 microcarriers with the best cell adhesion. Therefore, in the second step, no differences in the adhesion rates were observed under the agitation in the spinner compared to the static condition of the first step. However, the additional information collected, besides adhesion rates and cell growth, allowed us to eliminate 2 out of the 5 microcarriers for which significant differences in cell production by 7 days of culture were measured (in a range of 10 to 100-fold difference in cell concentration at the end of culture). No differences were observed among the other 3 microcarriers. To rationalize the time and cost, 2 microcarriers are selected for the scale-up in bioreactors. Cost is a significant factor in this decision, as there is approximately a fourfold difference in price per 100g between the most expensive and least expensive microcarriers. Therefore, discussions will be initiated to determine the two best candidates for scaling up in a bioreactor, taking into consideration both performance

Methodology :

The selection of microcarriers was initially investigated to meet the project's objectives. Comparative experiments were conducted to evaluate eight microcarriers based on three key factors: cell adhesion (adhesion rate and uniformity of colonization), cell growth (maximum specific growth rate, doubling time, and cell yield after seven days of culture), and cell detachment (rate of detachment during the harvesting step). The strategy involves three sequential steps: an initial pre-selection of microcarrier under static conditions, followed by a secondary selection in small-scale stirred conditions (100 mL), and ultimately, a final selection process that considers the scale of the bioreactor (1 L).

For in situ cell counting on microcarriers, the team relies on an offline monitoring method utilizing Dapi/methanol staining that allows to visualize the cell nuclei under UV light, while methanol eliminates all cells present in the sample. This customized technique uses the automated image processing method described by (Loubière 2018) to optimize the counting technique. In addition to cell counting, glucose, lactate, LDH, and NH3 levels within the culture media are measured during the process to monitor cell physiology.

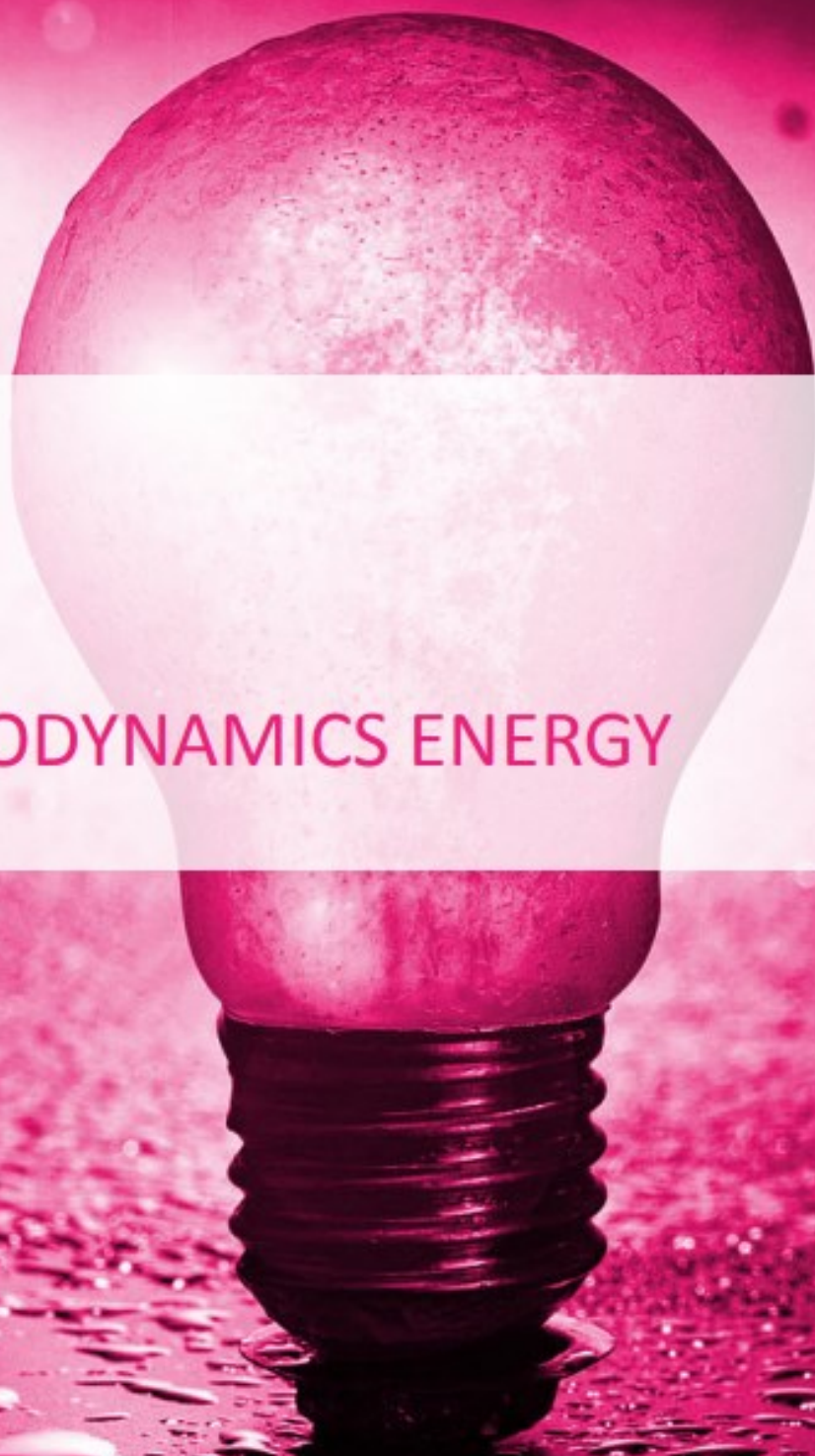
References :

Loubière, Céline. 2018. « Characterization and impact of the hydrodynamics on the performance of umbilical-cord derived stem cells culture in stirred tank bioreactors », 318.
Olsen, Timothy R., Kelvin S. Ng, Lye T. Lock, Tabassum Ahsan, et Jon A. Rowley. 2018. « Peak MSC—Are We There Yet? » *Frontiers in Medicine* 5 (juin): 178. <https://doi.org/10.3389/fmed.2018.00178>.

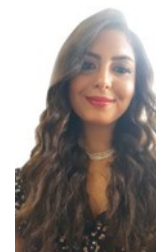


CITHERE

KINETICS THERMODYNAMICS ENERGY



LABORATOIRE
RÉACTIFS
ET GAZES
DES PROCESSUS



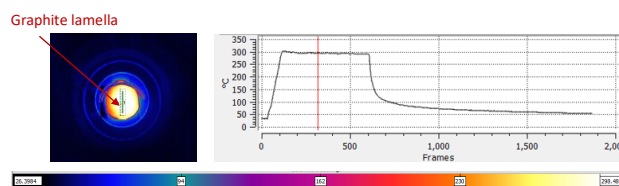
Keywords : Biomass, pyrolysis, bio-oil, biochar, fixed-bed reactor, laser, kinetic modeling

General context, scientific issues :

Fossil fuels have been a major source of energy for almost all the aspects of our lives. They have supplied more than 80% of the total world's energy consumption which has increased rapidly due to the population growth and the industrial development. Consequently, to overcome the resulting concerns of climate change and the depletion of the global fossil fuel that are endangering our future, renewable resources have attracted great interest in recent decades.

Biomass has proved itself to be a promising feedstock that can be converted into heat, electricity, valuable biofuels and biochemical products by different conversion processes. Notably, biomass pyrolysis has gained much attention since it is the initial step in other thermochemical processes (combustion and gasification) [1] and, depending on the operating conditions, it allows to produce different yields of bio-oil and biochar that can be transported and stored easily [2].

Illustration : Good homogeneity of temperature on the surface of graphite lamella while heating



Main results

A bibliographical review on different types of reactors used for the biomass pyrolysis has been done.

Although the majority of the studies focus on the heating rate and temperature during the biomass pyrolysis, understanding the effect of pressure on the occurring mechanisms is of great importance since the increase of pressure favors the formation of bio-char.

Due to the high thermal conductivity of graphite, a good homogeneity of the heating temperature is detected. This may enable to overcome the problem of huge thermal lags present in most of the fast pyrolysis micro-reactors [3]. The online analysis by SPI-MS that is combined to the laser device can be done effectively and softly. Since it dramatically reduces the fragment ions [4], it results in more interpretable mass spectra which helps in unraveling the chemical mechanisms during the biomass pyrolysis.

Objectives and stakes :

The aim of this study is to unravel and model the mechanisms of biomass pyrolysis based on advanced well-controlled experiments conducted on different types of real biomass particles and macromolecules of cellulose. Fixed and micro-fluidized bed reactors will be used and the effect of the operating conditions (temperature, pressure, heating rate, residence time of vapors) on the composition and the yields of products will be studied. A novel laser setup will also be used for pyrolysis, which will enable for the first time simultaneous online analysis of volatiles, and the imaging of temperature and particles.

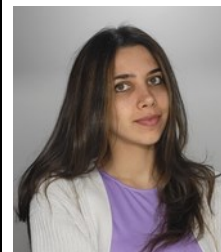
Methodology :

In the first part of the experimental work, by changing different parameters, a small amount of biomass is pyrolyzed in a vertical cylindrical stainless-steel fixed bed reactor connected to a Kammer valve that allows the measurement and the control of pressure. Other experiments are realized using a new laser pyrolysis device (developed by G. Parent and S. Becker from LEMTA). A thin film of cellulose or small particles of wood are laid over a graphite lamella that is heated by a powerful CO₂ laser (180 W) emitting an IR light at 10.6 μm . An advanced pyrometer is used to measure the temperature of the graphite lamella and therefore to control the power of the laser. In addition, the real-time temperature of the graphite lamella is measured thanks to an IR camera.

Throughout the work, different characterization techniques are used to analyze the resulting products: μ -GC for permanent gases, and NMR, FTIR, and SEM for biochar. The volatiles released from the fixed-bed pyrolysis are condensed and analyzed off-line by GC-MS, whereas those released from the laser pyrolysis are analyzed on-line by single photo-ionization mass spectrometry (SPI-MS). Moreover, the kinetics of macromolecules pyrolysis will be modeled in collaboration with Prof. M. Garcia-Perez in Washington State University.

References :

- [1] N. Brosse, A. Dufour, X. Meng, Q. Sun, and A. Ragauskas, "Miscanthus : a fast-growing crop for biofuels and chemicals production: A fast-growing crop for biofuels and chemicals production," *Biofuels Bioprod. Biorefining*, vol. 6, no. 5, pp. 580–598, Sep. 2012, doi: 10.1002/bbb.1353.
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- [4] Y. Le Brech, L. Jia, S. Cissé, G. Mauviel, N. Brosse, and A. Dufour, "Mechanisms of biomass pyrolysis studied by combining a fixed bed reactor with advanced gas analysis," *J. Anal. Appl. Pyrolysis*, vol. 117, pp. 334–346, Jan. 2016, doi: 10.1016/j.jaap.2015.10.013.

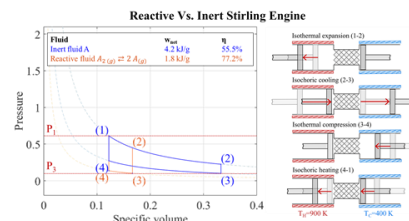


Keywords : Reactive working fluids, thermodynamic analysis, energy converters, energy efficiency, chemical equilibrium

General context, scientific issues :

The pursuit of more efficient and environmentally friendly energy converters has become crucial, particularly due to the increasingly stringent emissions targets and regulations. In an effort to improve the thermodynamic performance of energy converters, chemically reactive—rather than inert—working fluids are being investigated. These fluids enable the conversion of not only thermal energy, as in the case of conventional energy converters, but also chemical energy

Illustration : Comparison of pressure-volume diagrams: reactive fluid vs. inert fluid in a Stirling engine



Main results

Brayton cycle (isentropic compression, heat gain, isentropic expansion, heat rejection):

The net power obtained by a Brayton cycle working with reactive fluids is increased by more than 140% compared to that of the most efficient comparable inert fluid. Preliminary results also indicate that as the increase in power output rises, the increase in efficiency decreases.

Heat pump (isentropic compression, heat rejection, isentropic expansion, heat gain):

Results reveal a 212% increase in the coefficient of performance (COP) compared to an inert fluid system. However, there is a trade-off between the system's COP and the required mass flow rate needed to maintain the same heat supply in Watts compared to an inert heat pump.

Stirling engine (isothermal expansion, isochoric cooling, isothermal compression, isochoric heating):

It is observed that the utilization of chemically reactive working fluids introduces an additional degree of freedom to the ideal Stirling engine, specifically the possibility of nonadiabaticity in the internal regenerator. This means that an additional heat source or sink may be required during one of the isochoric processes. Results show that a range of reactive fluids offer an increase in thermal efficiency of up to 40%, but this comes at the cost of a 57% reduction in net specific work output of the cycle. Consequently, the mass flow rate of the cycle may need to be multiplied (up to 2.3 times) to ensure the same mechanical power output in Watts compared to an inert Stirling engine.

References :

- [1] S. Lasala, R. Privat, O. Herbinet, P. Arpentinier, D. Bonalumi, and J.-N. Jaubert, "Thermo-chemical engines: Unexploited high-potential energy converters," *Energy Conversion and Management*, vol. 229, p. 113685, Feb. 2021, doi: 10.1016/j.enconman.2020.113685.
- [2] A. Barakat, S. Lasala, P. Arpentinier, and J.-N. Jaubert, "The original and impactful exploitation of chemical energy in heat pumps," *Chemical Engineering Journal Advances*, vol. 12, p. 100400, Nov. 2022, doi: 10.1016/j.cej.2022.100400.

Objectives and stakes :

The two main objectives of this PhD thesis can be summarized as follows:

Investigating the thermodynamic effects of utilizing chemically reactive working fluids in energy converters like thermal engines and heat pumps.

Assessing the impact of utilizing reactive working fluids on the design of turbomachinery for energy converters.



Methodology :

In order to investigate the thermodynamic effects of utilizing reactive working fluids in energy converters, as a first step, a range of fictive reactive ideal gases is assessed. These gases are characterized by typical values of standard enthalpy and entropy of reaction, and they are based on equilibrated chemical reactions. Therefore, the thermodynamic transformations (compression, expansion, heat exchange, etc.) throughout the energy converter cycle induce a shift in the chemical equilibrium, leading to a new molar composition of the fluid for each temperature-pressure condition. The behavior of the reactive fluids is assessed in each unit of the energy converter, and the overall performance is evaluated and benchmarked against that of comparable inert working fluids.

The gas turbine engine [1], heat pump [2], and Stirling engine systems were investigated for various operating conditions and reaction stoichiometries.

All the calculations are carried out using Fortran codes developed by the authors.

On the other hand, the effect of utilizing reactive working fluids on the design of turbomachinery is performed using a MATLAB code that incorporates chemical transformations of the fluid throughout the thermodynamic cycle to assess the evolution of the velocity triangles

<p>2023</p> 	<p>Research subject: Development of an automatic generator of kinect data for the oxidation stability of biofuels</p> <p>Gabriel BATALHA DE SOUZA (1st year)</p> <p>Baptiste Sirjean, René Fournet</p> <p>CITHERE</p>	
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Keywords : Oxidation stability, biofuels, solvation, kinetic models

General context, scientific issues :

Currently, the combustion of fossil fuels is still the main source of energy used in several transport sectors, which is the main cause of global warming and the greenhouse effect. Therefore, biofuels would be an excellent alternative since they come from renewable sources and, in addition, the replacement by electric motors is very difficult or impossible in some cases, such as the aviation. However, biofuels are highly prone to aging due to the auto-oxidation phenomenon, which modifies their composition, physical properties, and can also generate harmful pollutants [1].

Main results

The benchmark is currently in progress to determine the best compromise between accuracy and calculation time. Current studies also show the complexity of these reactions, which involve Van Der Waals complexes. These complexes need to be taken into account for accurate calculation of the rate constants, particularly under the low-temperature conditions encountered in autoxidation. Moreover, the effect of viscosity and diffusion in the solvent must be considered.

Objectives and stakes :

The aim of this work is to develop an automatic generator of kinetics model for liquid phase oxidation, which is carried out using computer chemistry (ab initio/DFT with Gaussian and COSMO-RS software) and based on the correlation between the kinetic data in gas phase and the free energy of solvation. Finally, the liquid phase generator proposed will be integrated into the gas phase software already developed and widely used by

Methodology :

Currently, a benchmark study of theoretical kinetic modelling in liquid phase is being performed throughout the H-abstraction reaction between the t-butoxyl radical and the cyclohexane, cyclopentane, toluene, tetrahydrofuran and 1,3 dioxolane, as described in the Figure 1.

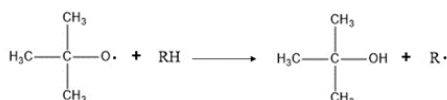


Figure 1. H-abstraction reaction of t-butoxyl radical

Firstly, the theoretical kinetics rate constants in gas phase based must be computed by coupling electronic structure calculations with the transition state theory (considering post-treatments such as tunneling effect and influence of hindered rotations). Afterward, the Gibbs free energies of solvation is calculated for a given solvent and temperature and it used to correct the rate constant previously obtained in gas phase, following Equation 1.


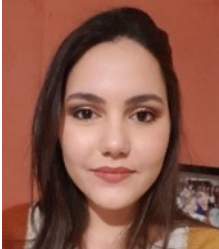
$$k_{liq} = k_{gas} \times \exp\left(-\frac{\Delta\Delta G_{solv}}{RT}\right) \quad (1)$$

Finally, the rates constants are fitted from the modified Arrhenius's law (Equation 2).

$$k = A \times T^n \times \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

References :

[1] Westbrook, C. K., Biofuels combustion. Annual review of physical chemistry 2013, 64, 201-219

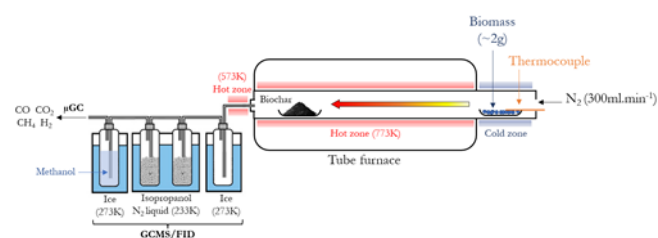
<p>2023</p> 	<p>Research subject: Pyrolysis of invasive plants to produce biochar and bio-oil: the case of Japanese knotweed (JKW)</p> <p>Manon Bechikhi (Engineer)</p> <p>Anthony Dufour</p> <p>CITHERE</p>	
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Keywords : Invasive plant, Pyrolysis, Biochar, Bio-oil

General context, scientific issues :

Japanese knotweed (JKW) is an invasive plant responsible for the fragility of our environment and infrastructure[1]. This invasive plant is present in many countries worldwide[2], where it causes many damages. At this moment, no method has proven to be effective eliminate it[3]. So, its use as a source of energy might be an answer to problems of treatment of green waste.

Illustration : Scheme of the experimental setup



Objectives and stakes :

This study is a new approach to recycling the huge amount of green waste generated each year by this invasive plant by producing products of interest (biochar, bio-oils, and gases) using a fast pyrolysis process.

Main results

JKW pyrolysis generates approximately 15, 30 and 55% of gases, biochar, and bio-oil respectively. The characterization of different fast pyrolysis products highlights the bio-oils richness in compounds of interest (hydrocarbon, alcohols, ...). Also, the composition of biochar focuses their use for soil amendment or active carbon. Indeed, for example, the leaves are composed of nitrogen, potassium and phosphorous which make it good fertilizer for the soil. This process of pyrolysis formed different gases: CO₂, CO, CH₄ and H₂. Finally, aluminum is observed at the rhizome surface (biomass and char) by EDX analysis. So, JKW can be considered as a metallophyte plant and a bioindicator of metals.

Methodology :

For this study, JKW was collected from two sites in Metropolitan Metz. It is divided into three parts: rhizome, stem, and leaf. These biomasses have been subjected to fast pyrolysis at 773K in a fixed-bed reactor under an inert atmosphere (continuous nitrogen flow). Bio-oils were collected by condensation, char were recovered in a quartz reactor. At the exit of the system, gases formed during the pyrolysis experiments were collected with a tedlar bag. The fast pyrolysis products (bio-oils, biochar, and non-condensable gas) have been characterized by physical and physicochemical techniques (GC/MS, FT ICR MS, XRF, SEM, EDX, μ GC, ...).

References :

- [1] Navratil, O. et al. Science of the Total Environment, 2021, 142995
- [2] Beerling, D.J. et al. Journal of Ecology, 1994, 959-979
- [3] Bailey, J.P. et al. Biol Invasions, 2009, 1189-1203



Keywords : biofuel, liquid phase oxidation, microchannels, kinetic study, Raman spectroscopy, in situ analytics, gas-liquid Taylor flow

General context, scientific issues :

Nowadays the increase of the share of biofuels in the transport sector, imposed by European regulations, requires studying their impacts on the liquid phase aging of conventional fuels in tanks. The thermal oxidation of liquid fuels stability of fuels is a key factor in the transportation and energy fields [1][2].

Objectives and stakes :

This project is a part of the ERC Bioscope, and the objective is to develop the experimental set-up to study the aging of biofuels and its consequences on their combustion characteristics (reactivity, pollutants). A microchannel reactor will be used to carry out the experiments on the aging of liquid. These liquid-phase oxidation experiments will be coupled with an ideal gas-phase combustion reactor. Analytical methods will also be developed to monitor the kinetics of aging and combustion (Raman, HPLC, GC).

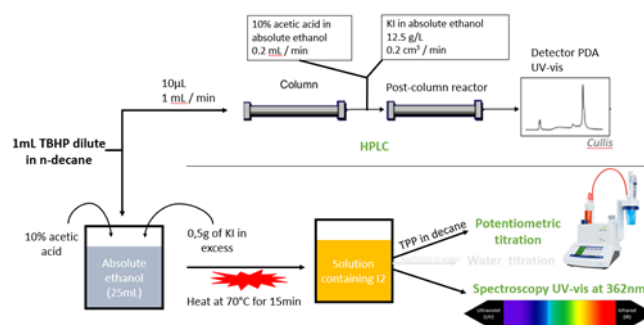
Methodology :

The reactant used as a surrogate fuel is n-decane. For surrogate biofuel, different molecules of each oxygenated family will be used; TBHP (terbutyl hydroperoxide) is used as the ROOH source.

First, the analytical part is studied. Indeed, the main factor of stability of liquid fuel is its peroxide concentration. The standardized method using iodometric titration in an aqueous solution is known to be little reproducible [1]. The iodometric method in an organic solvent is used and compared to the method conducted in an aqueous solvent. Cullis and al. used an HPLC (high-performance liquid chromatography) to precisely determine ROOH concentration [3]. The methodology is detailed in the illustration part.

Hydrodynamic and process parameters are studied concerning the microchannel reactor to determine the optimal conditions for the future pilot.

Illustration : Analytical Techniques



Main results

The quantification of peroxide by iodometric titration, in organic solution, shows an improved reproducibility and a detection range more interesting for our purpose.

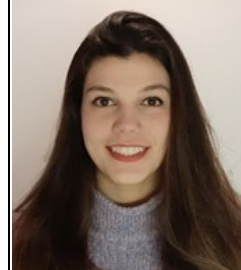
This HPLC setup quantifies ROOH in solution by determining the concentration of I_2 using an easy and reproducible method. The coupling of the iodometric technique in an analytical apparatus such as HPLC enables the detection of very low concentrations of hydroperoxides



Figure 1: Chromatogram of TBHP diluted in iso-octane 104 times detected at 362nm.

References :

- [1] West ZJ. Studies of Jet Fuel Autoxidation Chemistry: Catalytic Hydroperoxide Decomposition & High Heat Flux Effects. Doctoral dissertation, University of Dayton, 2011
- [2] Jia T, Zhang X, Liu Y, et al. A comprehensive review of the thermal oxidation stability of jet fuels. Chem Eng Sci. 2021;229.
- [3] Cullis C. F., Hirschler M. and Rogers R. L. ,1981, The oxidation of decane in the liquid and gaseous phases Proc. R. Soc. Lond. A375543–563



Keywords : Kinetics, automatic generation of rate constants, transition state models, *ab initio* calculations

General context, scientific issues :

Biofuels are a solution for low-emission combustion systems; however, they have poor resistance to liquid phase oxidation. The thesis is part of the BioSCOPE - ERC project that investigates the aging of alternative fuels in the liquid phase. Reaction mechanisms describing the chemical conversion of these fuels are essential tools to understand this phenomenon [1]. The mechanism describes hundreds of species and thousands of reactions for which accurate thermochemical and kinetic data are necessary [2].

Objectives and stakes :

The main objective of the thesis is to contribute to the development of automatic generators of kinetic models to describe biofuels oxidation by improving the accuracy of the kinetic data through two main approaches:

- Create tabulated transition state (TS) models for the kinetic rate rules of different reaction classes;
- Develop algorithms to automatically calculate the thermo-kinetic data related to these rate rules.

Methodology :

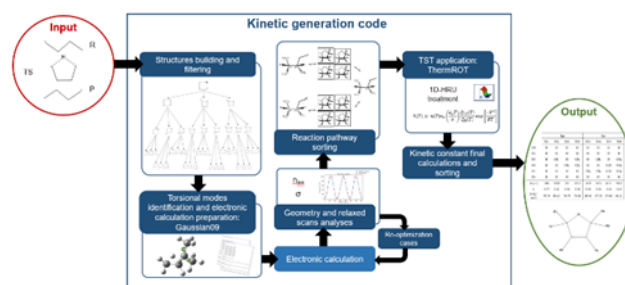
The reaction kinetics are calculated theoretically using *ab initio* methods and the transition state theory (TST), resulting in a modified Arrhenius expression. The first reaction class investigated during the thesis were the H-shift reactions of alkyl radicals [3], for which a first study indicates the impact of radical branching level on the kinetic rates. This study also suggests that a generic alkyl substituent can be represented by a methyl substituent.

Based on these results, a table with TS models was proposed to be used as a reference for the kinetic rules applied for this reaction class in reaction mechanisms. These tables included reactions passing through transition states with 4 and 5 members in the ring.

In order to expand the rules for TS with 6 members, a code in Python was written to automatically generate the reaction rates. The code starts by creating all the possible substituted radicals and transition state structures based on non-substituted structures. These 3D structures are then automatically submitted to the *ab initio* calculations. Once the results of *ab initio* calculations are finished, the code retrieves and organizes all the required information for the transition state theory (TST) application. It runs the TST software, recover the kinetic rates, and organizes them in a table that can be directly applied to reaction mechanisms.

Illustration :

Title: Scheme of the code developed to automatically calculate the rate rules.





Main results

The code was applied for the calculation of H-shift reaction rates for transition states passing through a 4-members cycle. The results produced by the code were compared with the previous studies, for which the calculations were manually launched. For most part of the reactions, the kinetic constants were similar, with differences of less than 20% at low temperatures. For some cases, however, the code was able to identify the number of isomers and symmetries on structures more accurately than the manual evaluations, which exemplifies the importance of automatization for improving the precision of data. The code is flexible to generate tables of TS models for other reactions classes, such as beta-scissions and H-abstractions

References :

References

- [1] M. D. et al, J. Phys. Chem. B. 2021, 125: 6955-6967.
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- [3] F. Citrangolo Destro et al., Proc. Combust. Inst. 2022, In press

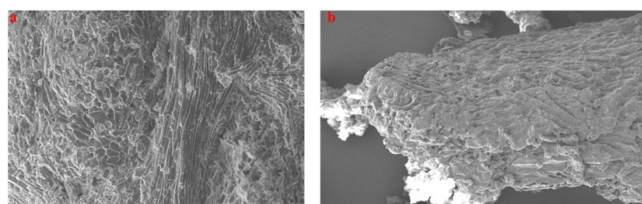
<p>2023</p> 	<p>Research subject: Hydrothermal carbonization of Moroccan two-phase olive mill wastes: effect of reaction time and temperature</p> <p>Akram Dahdouh (3rd year)</p> <p>Yann Le Brech, Anthony Dufour</p> <p>CITHERE</p>	
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Keywords : Hydrothermal carbonization, olive mill wastes, temperature, reaction time

General context, scientific issues :

Olive oil industry generates annually more than 30 million m³ of solid (olive pomace), semi-solid (two-phase olive mill waste) and liquid (olive mill wastewater) wastes. The absence of an effective end of pipe treatment to treat these by-products may be detrimental for the environment especially in the producing countries. In fact, wastes from olive oil industry can be very polluting due to their high phenol content, acidic properties, and high organic load (Dahdouh et al., 2023). Additionally, their high moisture >40 % content make their conversion via the conventional technologies (i.e., pyrolysis and combustion) not efficient energetically due to the necessity of drying. Therefore, hydrothermal technologies, such as liquefaction, carbonization and gasification can be considered as promising solution to deal with these effluents (Gimenez et al., 2020).

Illustration : SEM images of the raw biomass (a) and the produced hydro-char at 250°C(b)



Objectives and stakes :

The aim of this study is to assess the conversion of wet olive oil waste of Moroccan origin, two-phase olive mill waste, by hydrothermal carbonization into solid fuels. This work deals, first, with the characterization of the raw materials used, then with the understanding of the effect of the operating parameters (time and temperature). The resulting products (hydro-chars, aqueous phase and gas) will be characterized by different techniques to identify the operating parameters effects on the prod-

Main results

This study highlighted the impact of reaction temperature and time on the hydrochars composition and quality. Results have shown that reaction time variation had no significant effect of the products yields and composition. Compared to the raw biomass, the morphology of the produced hydrochars was more porous after the treatment. Concerning the hydrochars energy content, HHV value reached its maximum (30 MJ/kg) value at 250°C and 3 hours reaction time. Additionally, FTIR spectroscopy showed that the obtained hydrochars are rich in functional groups (C-H, O-H, C-O, and aromatic C=C).

Methodology :

After the characterization of the raw biomass (volatile matter, ash content and fixed carbon, elemental analysis, FTIR spectra). Hydrothermal carbonization (HTC) tests were performed in a 300mL batch reactor using water as solvent. A variation of the process operating parameter was conducted to evaluate the effect of temperature, reaction time on the products yields and quality. The obtained products were analyzed with different techniques (Elemental analysis, Total organic carbon (TOC), Thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR)), Scanning electron spectroscopy (SEM) and Nuclear Magnetic Resonance spectroscopy.

References :

- Dahdouh, A., Khay, I., Le Brech, Y., El Maakoul, A., Bakhouya, M., 2023. Olive oil industry: a review of waste stream composition, environmental impacts, and energy valorization paths. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-023-25867-z>
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Keywords : Wood combustion, inset, heat transfer, modeling, soot, pollutants

General context, scientific issues :

Even though it provides an affordable and efficient solution based on renewable fuels, biomass based domestic heating appliances are a significant particle matter emitter, if left uncontrolled

Objectives and stakes :

The objective of this work is to study the influence of each parameter (such as wood type, moisture content, and fireplace geometry), in order to reduce these polluting emissions and to increase the efficiency of wood combustion in an inset.

This will be achieved by creating a method to simulate, in detailed chemistry, the combustion inside a wood heating appliance.

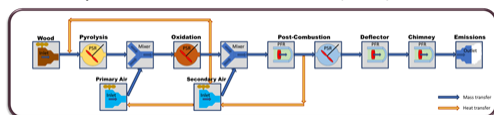
Methodology :

BioPOx — Detailed chemistry and its kinetics
ERN — Aerodynamics
— Transfer of mass and heat



BioPOx1,2: BioPOx is a kinetic chemical model with more than 700 species and 12000 reactions, it is formed by: ① A semi-detailed mechanism to describe the devolatilization of biomass³. ② A detailed mechanism for the combustion of the produced tar (in the gas phase). It was developed in a previous study and modified in the present to contain new chemical species and more precise results. ③ A soot model, simulating the formation and oxidation of soot. ERN: The aerodynamics and mass and heat transfer phenomena inside the wood inset are simplified by the ERN (equivalent reactor network), which is formed by: PSRs (perfectly stirred reactors) and PFRs (plug flow reactors). represented in Figure 1.

Figure 1: The Equivalent reactor network (ERN)



Using the experimental results from CSTB, obtained from combustion tests on hornbeam logs in an inset, the ERN-BioPOx model (gas phase) was validated. Figure 2 below shows examples of comparisons between numerical and experimental results for the emissions of levoglucosan, PAHs and BTEX, at the chimney outlet.

Figure 2: Numerical and experimental results for some of the emissions

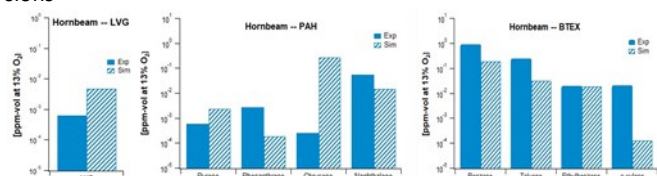
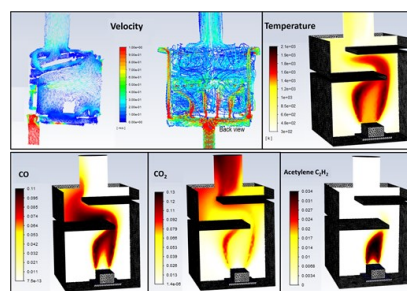


Illustration : Back view of the 3D meshed structure showing the velocities inside the inset (up-left). A 2D plane view of a burning log inside the wood inset colored by temperature (up-right). A 2D plane view of the mole fractions of CO, CO₂ and C₂H₂ (down).





Main results

At the same time, CFD studies were conducted with ANSYS Fluent to better understand the aerodynamics and the heat and mass transfers, and thus better represent them in a new optimized ERN. As shown in Figure 3, two meshes are used: a first mesh, very detailed and complex, used for cold simulations; and a simplified mesh, suitable for the coupling with a simplified chemical model. This figure shows the cold air velocity field in the detailed mesh (left), and the temperature distribution inside the inset, in the simplified mesh (right). Figure 4 shows the distribution of the mole fraction of CO, CO₂ and acetylene. In the simulations using the simplified mesh, where chemistry is introduced, the wood log is modeled as a fixed-dimensional cuboid, and the upper surface of the log is considered the fuel inlet. The air inlets are reduced to the two main inlets: under the log and at the back of the inset. The chemical model used in these CFD simulations, is developed by Maoqi Lu et al., contains around 100 chemical reactions and focuses on the oxidation of methane.

References :

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<p>2023</p> 	<p>Research subject: Combustion performances of biofuels resulting of Enzymatic Hydrolysis Lignin</p> <p>Nicolas Delort (3rd year)</p> <p>Frédérique Battin-Leclerc, Olivier Herbinet</p> <p>CITHERE</p>	
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Keywords : Biofuel, lignin, combustion, flame, modeling, oxygenated aromatics

General context, scientific issues :

In a context of global warming and exhaustion of fossil sources of energy, sobriety and new technologies will allow the energy transition and to reach carbon neutrality. Transport is one of the larger emitters of greenhouse gas: 25% in 2019; 29% of final energy is consumed in this field [1]

Objectives and stakes :

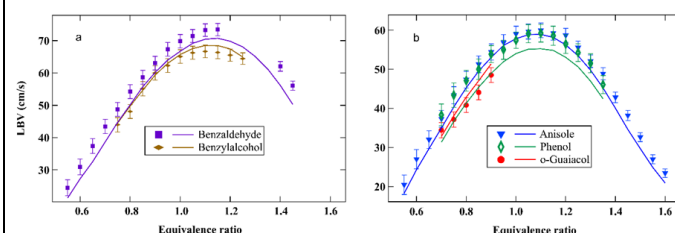
The European project EHLICATHOL [2] aims to develop a new kind of 2G biofuel synthesized from enzymatic hydrolysis lignin, a waste of 2G bio-ethanol refineries. It gathers academic partners (AALTO, LIKAT, EPFL, NTNU, TU/E, LRGP-CNRS) and an industrial partner (Vertoro). Our team in Nancy is in charge of the combustion study with experimental and numerical works.

Methodology :

The methodology is first to work on individual biofuel compounds, arenes and oxygenated aromatics. These oxygenated species are slightly studied in literature and only anisole was studied in flame. Representative mixings of the biofuel will be then studied. The main tasks on which I am involved are the measurement of Laminar Burning Velocities (LBV) and the development of a detailed kinetic model:

- LBV measurements with a flat flame burner at atmospheric pressure using the heat flux method [3]. Experiments are performed on a wide range of equivalence ratios for various fresh gas temperatures. This facility has been improved to face issues due this biofuel properties [4]; its main advantage is the direct way to obtain the LBV value.
- the development of a detailed kinetic model, named COLIBRI, allows to model the combustion on Chemkin Pro. It is mainly built merging the most precise existing models for each compound of interest.

Illustration : Comparison between simulated and measured LBVs of a) benzaldehyde and benzylalcohol, b) anisole, phenol and guaiacol




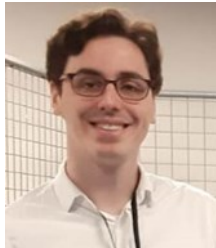
Main results

The LBV measurements were performed for 7 neat arenes (toluene, xylene isomers, styrene, 1,2,3- and 1,2,4-trimethylbenzene) and 9 neat oxygenated aromatics (phenol, benzaldehyde, anisole, benzylalcohol, the three cresol isomers, 2-phenylethanol, and o-guaiacol). Concerning the obtained data on oxygenated aromatics, measurements are performed for a fresh gas temperature of 398K due to their low volatility. Benzaldehyde has the highest LBV, up to 70 cm/s, and p-cresol the lowest one. The isomers of xylene have almost the same LBV, it's also the case for trimethylbenzenes, but not for cresols for which ortho and para isomers have a LBV about 10 cm/s higher than para-cresol.

As it is shown in Figure 1, there is an overall good agreement between experimental and numerical results. Sensibility and flux analyses are performed and highlight the key role of cyclopentadienone and of resonantly stabilized radicals: phenoxy, phenyl and hydroxyphenoxy in the combustion process

References :

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- [2] <http://ehlicathol.eu/>
- [3] K.J. Bosschaart, L.P.H. de Goey, The laminar burning velocity of flames propagating in mixtures of hydrocarbons and air measured with the heat flux method, *Combustion and Flame*. 136 (2004) 261–269. <https://doi.org/10.1016/j.combustflame.2003.10.005>.
- [4] F. Battin-Leclerc, N. Delort, I. Meziane, O. Herbinet, Y. Sang, Y. Li, Possible use as biofuels of monoaromatic oxygenates produced by lignin catalytic conversion: A review, *Catalysis Today*. 408 (2023) 150–167. [doi:10.1016/j.cattod.2022.06.006](https://doi.org/10.1016/j.cattod.2022.06.006).

<p>2023</p> 	<p>Research subject: Kinetic modelling of the impact of oxygenated fuels on pollutant emissions in spark ignition engines</p> <p>Timothée Fages (2nd year)</p> <p>Pierre-Alexandre Glaude, René Fournet</p> <p>CITHERE</p>	
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Keywords : Gasoline, alcohol, soot, biofuels

General context, scientific issues :

Gasoline engines will still account for at least 50 % of light duty vehicles over the next decade. However, Direct Injection Spark Ignition (DISI) gasoline engines, despite providing fuel economy, emit a large amount of soot. Moreover, the EU favors the use of oxygenated biofuels which tend to reduce soot but increase aldehydes and NO_x emission. This study aims to predict those pollutants.

Objectives and stakes :

The purpose of this project is to model and simulate soot and pollutants formation from biofuels when used in DI-SI engines to inform the development of a low emission motor. The detailed kinetic model of the oxygenated gasoline combustion should be able to predict the main combustion parameters and formation of aldehydes, NO_x and soot precursors (polycyclic aromatic hydrocarbons - PAH).

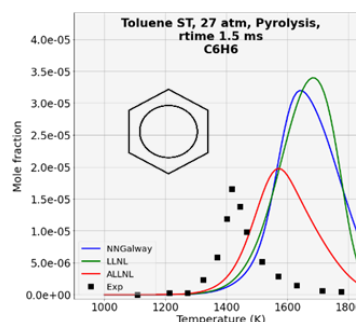
Methodology :

The oxygenated gasoline will be modeled with isooctane, n-heptane, toluene and either ethanol or isobutanol to make it computationally usable.

Different kinetic models from the literature will be tested, modified, and reduced through the utilization of the Ansys Chemkin-Pro software or the Cantera Python module. This will comprise:

- The comparison between experimental and simulated ignition delay times (IDT) in a shock tube.
- The comparison between experimental and simulated species profiles (SP) in a burner, a shock-tube or in a plug flow reactor.
- The comparison between experimental and simulated burning velocities (BV) in a burner.
- The study of reactions sensitivity and reactions paths between models.
- The fusion and modification of different models through homemade code, whenever required.
- The improvement of the model with quantum calculations

Illustration : Simulated toluene species profiles (SP) of benzene relative to experimental results in a shock tube.



Main results



Among the various models reviewed, two models have been heavily changed:

1. NUIGMech1.2[1] (Galway): The low temperature of the mechanism has been removed (HGalway) and a sub mechanism of high temperature isooctane has been added.
2. LLNL Gasoline Surrogate[2]: A more updated aromatic sub-mechanism from LLNL (Alkylaromatic2.1) has been fused with the LLNL mechanism giving the new mechanism ALLNL-V2.

Over the range of IDT (821 experimental points), the best mechanism seems to be the Galway mechanism. However, its size is problematic. HGalway has a reduced accuracy (as expected when reducing a model) and still a heavy weight with over 9000 reactions and 2000 species. As such, while still performing, it may not constitute the best candidate for future and heavier simulation. Other less performing but smaller models such as LLNL (6000/1400) and ALLNL-V2 (6500/1500) have relatively close results and have not yet been reduced. As far as SP results are concerned, ALLNL-V2 and HGalway are equivalent, while LLNL performs worse. Due to its size, ALLNL-V2 appears to be the most consistent model overall, but this may change with subsequent modifications to the other models.

References :

- [1] Martinez S, Baigmohammadi M, Patel V, Panigrahy S, Sahu A B, Nagaraja S, Ramalingam A, Heufer K A, Pekalski A, Curran H J 2021 Combustion and Flame 234 111626
- [2] Mehl M, Pitz W J, Westbrook C K, Curran H J 2011 Proceedings of the Combustion Institute 33 193

<p>2023</p> 	<p>Research subject: Physicochemical qualities and potential for the recovery of biochar produced by pyrolysis</p> <p>Eya GHOMRI (engineer)</p> <p>Yann LE BRECH</p> <p>CITHERE</p>	
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Keywords : Biomass, Pyrolysis, Biochar, Soil-amendment, Characterization

General context, scientific issues :

The development of the biomass-energy sector associated with the reduction of hexagonal expenditure towards fossil resources and the desire to preserve the long-term fertility of soils by substituting non-renewable organic materials in crop supports leads to a craze of biomass managers (farmers, fertilization and energy manufacturers) towards the development of pyrolysis technology. Indeed, the transformation of biomass (wood, crop residues, etc.) into charcoal is an opportunity to sequester carbon [1] and improve soil fertility [2], without major changes in cultural practices.

Objectives and stakes :

The project entitled QUALICHAR funded by ADEME (French Agency of Environment and Energy Management) focuses on the valorisation of selected conventional lignocellulosic biomasses (LBs) (Oak, Douglas, Pectin fir, Beech, Spruce), Crop residue (Corn raids) and unconventional biomasses (UB) (Digestate, Poultry Droppings and Cattle manure) into biochars by pyrolysis in order to assess their agro-environmental as function of their physical and chemical properties.

Methodology :

In this study, characterizations of biochar, produced in a tubular furnace under flushing inert gas at two different temperatures (500 and 800°C) for slow (10°C/min) and fast (~1°C/s) pyrolysis is done. Indeed, the fate of organic material (mainly carbon structure) and inorganic material are studied by various characterization techniques (FTIR, Raman, BET surface area, Ultimate and Proximate analysis, Scanning Electron Microscopy - EDX, 13C solid-state NMR, Calorimetry).

Main results

Biochars from LBs exhibit conventional composition and structures (i.e. for biochars at 800°C: ~95%wtC, ~85%wt fix carbon, HD/HG=0.75 in Raman spectroscopy, ~220 m²/g BET surface area). Concerning UB and crop residue, the composition and structure present a significant heterogeneity mainly due to high initial mineral content. Primary results on these biochars show that the fate of mineral content (i.e. P, Ca, Si, Mg, Na) is function of temperature treatment (Figure 1). For instance, due to the temperature increase, Silica particle tends to agglomerate in crop residue and minerals (especially Na) agglomeration is observed for biochar from digestate. The structure and shape of minerals in crop residue and unconventional biomasses will determine their agro-environmental (i.e. Impact on Nitrogen volatilization and Phosphorous bioavailability) potential but also could lead to high-added value application (Catalyst, Adsorbents).

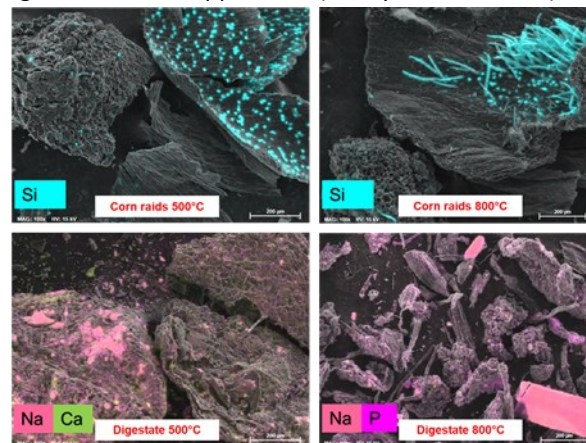




Figure 1: Scanning Electron Microscopy (MEB) coupled with Energy Dispersive X-ray (EDX) analysis of Corn raids and Digestate biochar produced at 500 and 800°C by fast pyrolysis process.

References :

- [1] Sohrab Haghighi Mood, Manuel Raul Pelaez-Samaniego, et Manuel Garcia-Perez, « Perspectives of Engineered Biochar for Environmental Applications: A Review », *Energy & Fuels* 36, no 15 (2022): 7940-7986, <https://doi.org/10.1021/acs.energyfuels.2c01201>.
- [2] Kathrin Weber et Peter Quicker, « Properties of Biochar », 2018, *Fuel*, <https://doi.org/10.1016/j.fuel.2017.12.054>.

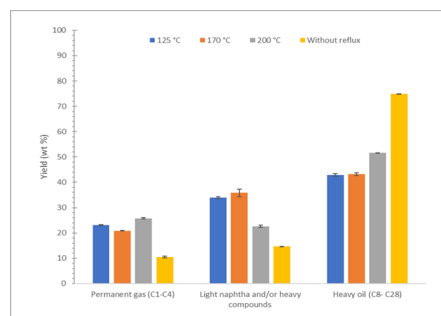
<p>2023</p> 	<p>Research subject: Analysis and study of the pyrolysis of plastic waste: experimentation and modeling</p> <p>Nabil Hassibi (3rd year)</p> <p>Guillain Mauviel, Valérie Burklé-Vitzthum</p> <p>CITHERE</p>	
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Keywords : Pyrolysis, plastic waste, reflux, modeling

General context, scientific issues :

The amount of plastic consumption is increasing every year worldwide. The waste generated by their production, transportation and disposal creates various environmental problems. Within the different ways of using plastic waste, pyrolysis seems to be an attractive and environmentally friendly possibility for a sustainable use of waste in the long term [1], [2]. The products obtained by the pyrolysis of plastics depend generally on the evolution of the temperature of the plastics, the use of reflux, the type of reactor, the pressure, the residence time of the solid and the gas, the catalysts, the type and the ratio of carrier gas flow to the plastic flow [3].

Illustration : Effect of the reflux temperature on product yields issued from PP pyrolysis at various temperatures of reflux (125–170–200 °C) and without reflux.



Objectives and stakes :

The goal of this PhD is to manage plastic waste by pyrolysis, with the aim of recovering and valorizing the products. To this end, a pyrolysis pilot with reflux has been developed to increase and optimize the production of light hydrocarbons, which are interesting to recover as raw materials or fuel. In order to model and optimize the reactor, it is necessary to consider an equilibrium model between the gas phase and the liquid phase (biphasic reactive environment) coupled with a kinetic model of radical cracking (for polyolefins), without forgetting to consider heat and matter transfers because the time scales of these can be close to those of the reaction kinetics. The modelling component will be developed using a MATLAB code and will comprise several stages. The molar mass distribution (polymer chain length distribution) will be completely reconstructed by the kinetics of Monte Carlo.

Methodology :

The experimental work related to this thesis started on a small, well-controlled reflux semi-batch reactor with a polyolefin (polypropylene, polystyrene), before working on a semi-industrial pilot. These tests are performed at various conditions (pure or mixed polymer, heating power, inert gas flow). The various products are characterized (gas by online micro-GC, oils by GC-FID-MS and FT-ICR-MS). In particular, the pyrolysis of polypropylene (PP) was investigated using a semi-batch, vertical glass reactor heated at 480 °C equipped with a reflux condenser [4]. The pyrolysis was performed with and without a reflux condenser. The temperature at the top of this reflux condenser was ranged from 125 °C to 200 °C

Main results

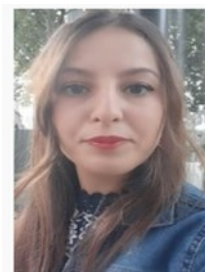
The pyrolysis results showed that the use of a reflux condenser influenced strongly the PP decomposition. Propylene is the main gas detected in all experiments, followed by butadiene. The characterization of liquid products achieved by GC-MS/FID showed that the major compound produced was C9 with a mass fraction of 71.2 wt% at 125 °C of reflux temperature. The characterization of liquid products by FT-ICR MS confirmed the importance of the use of a reflux to control products composition by showing that the hydrocarbons compounds issued from the pyrolysis without reflux can reach 65 carbons unlike the hydrocarbon compounds issued from the pyrolysis with reflux that do not exceed 35 carbons, even if the temperature range between 125 °C and 200 °C did not have that much influence on the distribution of the products.

Conclusion

The molecular weight distribution of hydrocarbons can be narrowed when the reflux is used and it can be possible to produce hydrocarbons with a narrow distribution of light molecular weight (MW) compounds which are more highly valuable. Consequently, the molecules of interest are maximized, especially those corresponding to the naphtha cuts (hydrocarbons molecules that comprise 5 to 12 carbon).

References :

- [1] N. Kiran, E. Ekin, et C. E. Snape, « Recycling of plastic wastes via pyrolysis », Resources, Conservation and Recycling, vol. 29, no 4, p. 273-283, 2000.
- [2] O. Dogu et al., « The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions », Progress in Energy and Combustion Science, vol. 84, p. 100901, 2021.
- [3] W. Kaminsky, « Possibilities and limits of pyrolysis », Makromolekulare Chemie. Macromolecular Symposia, vol. 57, no 1, p. 145-160, 1992.
- [4] N. Hassibi et al., « Analysis and control of products obtained from pyrolysis of polypropylene using a reflux semi-batch reactor and GC-MS/FID and FT-ICR MS », Journal of Analytical and Applied Pyrolysis, vol. 169, p. 105826, 2023.



Keywords : combustion, oxidation, enzymatic hydrolysis lignin, bio-oils, Jet-stirred reactor, kinetic study

General context, scientific issues :

LRGP-CNRS is involved in the EHL CATHOL project since November 2020 [1]. EHL CATHOL is a European project that aims to develop a new kind of second-generation (2G) biofuel synthesized from Enzymatic Hydrolysis Lignin (EHL), a by-product of 2G bio-ethanol refinery. These liquid fuels are intended to be used as alternative fuels, as they are generated from renewable and sustainable sources with a low CO₂-emission. To achieve the objectives of this project, I perform laboratory experiments and develop kinetic models.

Objectives and stakes :

The goal of this PhD is to study in the gas phase the oxidation the most important chemical species included in EHL-derived solvolysis, in order to produce a new set of experimental data.

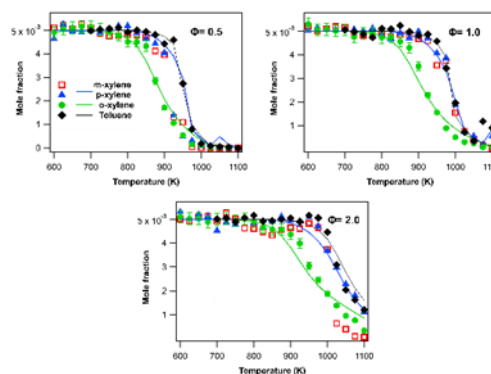
Methodology :

The oxidation experiments were carried out in a jet-stirred reactor (JSR), over a temperature range of 600 to 1100 K. The fuel-air equivalence ratio, (Φ), was fixed at three values (0.5, 1 and 2), and the pressure was set at 1.067 bar. The gas leaving the reactor was transported through a heated line at 420 K to gas chromatographs with MS and FID detection, in order to quantify a wide range of products.

Among the species formed by the catalytic conversion of EHL, the oxidation of ten of them (toluene, the three isomers of xylene, the three isomers of cresol, phenol, styrene and guaiacol) was studied experimentally.

Main results

Figure 1: Experimental and predicted temperature evolutions of the mole fractions of toluene and the three isomers of xylene at $\Phi=0.5, 1$ and 2 . Error bars are only displayed for o-xylene.



The experimental results obtained in this study and presented in Figure 1 showed that, as suggested by Kukkadapu et al. [1], p- and m-xylenes have a similar reactivity close to that of toluene whereas that of o-xylene is significantly more reactive, since it starts to react at a temperature of about 100 K lower than the 3 other fuels. This difference of reactivity is very well reproduced by simulations using the COLIBRI model developed in this study by my colleague Nicolas Delort. Main common products were CO, CO₂, benzene, ethylbenzene, benzaldehyde, and benzofuran. Phthalan, a cyclic ether linking the two alkyl branches was only quantified for o-xylene, as it is a product specific to its oxidation, as proposed by Roubaud et al [2] during their work in a rapid compression machine.

References :

- [1] G. Kukkadapu, D. Kang, S.W. Wagnon, K. Zhang, M. Mehl, M. Monge-Palacios, H. Wang, S.S. Goldsborough, C.K. Westbrook, W.J. Pitz, Kinetic modeling study of surrogate components for gasoline, jet and diesel fuels: C7-C11 methylated aromatics, *Proceedings of the Combustion Institute*. 37 (2019) 521–529. <https://doi.org/10.1016/j.proci.2018.08.016>.
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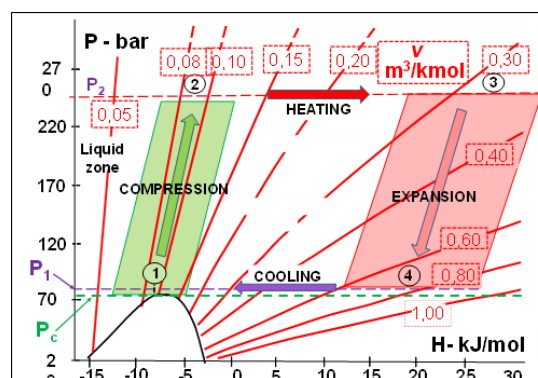


Keywords : Thermodynamics, Energy, Power generation, Supercritical cycles

General context, scientific issues :

Conventional electrical plants consume fossil energies and generate massive CO₂ emissions. Although gas turbines combined cycles (GTCC) have passed the 62% efficiency mark and are capable of burning pure hydrogen, their decarbonation remains a puzzling issue. There is an increasing interest placed on "sCO₂ (power) cycles" which involve supercritical CO₂ as driving fluid. While closed Brayton sCO₂ cycles can efficiently utilize residual heat fluxes, semi-closed ones offer the possibility of directly capturing CO₂.

Illustration : Sketch of a typical sCO₂ Brayton closed cycle



Objectives and stakes :

The main motivation underlying the thesis work is that the thermodynamics of "real fluids" - and in particular of supercritical ones - makes it possible to minimize the mechanical energy consumed in compression stages and maximize that produced in expansion stages. The thesis objective was then to analyze the assets and drawbacks of some most propitious Rankine and Brayton sCO₂ as possible routes towards a zero CO₂ emission power sector.

Main results

- 1- A Review of the most sCO₂ technology aspects has been made.
- 2- Regarding Rankine cycles: Given the modest level of the critical temperature of CO₂ (31°C) and considering future hotter climates, we tried to raise the condensation temperature of pure CO₂ to 45°C by adding a third, environmentally acceptable molecule but such attempts proved unsuccessful.
- 3- Regarding closed Brayton cycles:
 - High efficiencies can be reached by performing the compression steps close to the critical point, given that the expansion steps are also efficient as they are performed in the higher enthalpy field.
 - Although CO₂ features a moderate critical pressure (73 bar), one must use modest compression ratios, to keep a reasonable level for the final pressure (e.g. £ 225 bar). This requires sCO₂ Brayton cycles to comprise efficient thermal "regenerative" steps to recover the heat available at turbine discharge.
 - Brayton sCO₂ cycles achieve attractive performances when simple heat transfers from the heat source are feasible.
 - However, when they require multiple thermal exchangers, they are outperformed by conventional two-pressure steam cycles, the technology of which is well established.
 - Moreover, the implementation of sCO₂ power cycles is still at a relatively early stage of maturity.

Methodology :

To evaluate the merits and shortcomings of sCO₂ Cycles, we have determined the efficiencies of various sCO₂ configurations through thermodynamic simulations, using specialized software resources, and compared them with those of conventional plants. The input data for those simulations were chosen to reflect the hotter climates of the future. To that end, we have purposely selected heat sinks having relatively high temperatures (45°C) to enable covering most regional climates conditions. Different cycle's configurations were explored, viz. Rankine and Brayton cycles, implying different heat introductions and heat regeneration devices.

References :

- [1] M. Molière, "The Fuel Flexibility of Gas Turbines: A Review and Retrospective Outlook", paper accepted for publication in Energies.
- [2] M. Molière, F. Geiger, R. Privat and J-N. Jaubert, "Emerging Thermodynamic Cycles and Thermal Power Generation", Proceedings of ECOS 2022, 35th International Conference, Copenhagen, 2022 July 3-7.

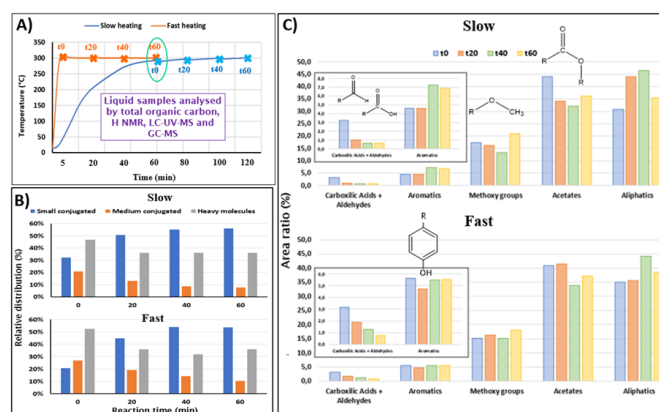


Keywords : Spruce bark, hydrothermal treatment, phenolic compounds, Benchtop 1HNMR, UV fluorescence.

General context, scientific issues :

ECO-VALUE project financed by the Carnot Ic el institute and the European Union aims to valorise barks considered as wood by-product using hydrothermal treatment. The originality is to compare fast (induction) and slow heating systems

Illustration : Evolution of A) temperature in the liquid phase vs. time; Relative distribution of B) small, medium size and heavy conjugated molecules (UV Fluorescence) and C) main moieties in aqueous phase (1H NMR).



Objectives and stakes :

(1) Comparison of the chemical transformations of spruce bark by studying the mass transfers during hydrothermal treatment for 1h, (2) studying the effects of fast (induction) and slow heating rates on the chemical conversions, (3) using original analytical techniques to identify and quantify produced chemicals.

Main results

Fast heating system allows to reach 300°C after 5 minutes compared to 60 minutes using slow heating system (Fig A). UV fluorescence results (Fig B) shows that there is no difference in relative composition of the aqueous phase based on Fluorescence UV analysis. The main difference is observed at t0, indeed small conjugated molecules relative distributions is higher for slow heating. That means that depolymerisation at t0 is more important for slow heating. Samplings at 0, 20, 40 and 60 minutes were analysed by 1H NMR 60MHz benchtop with water saturation. Based on 1H area ratios (Fig C), composition of aqueous phase is similar for fast and slow heating at different sampling times. However, the carboxylic acids and aldehydes degradation kinetics is faster for slow compared to fast heating (between t0 and t20).

Methodology :

Hydrothermal treatment of spruce bark was performed at 300°C for 1h in 0.3L autoclave. In this study, slow and fast (induction system) heating were applied. Sampling was done each 20 minutes to follow-up the chemical conversion of lignin and carbohydrates during the process.

Liquid products were analysed by: LC-UV-MS, 1H-NMR, TOC and UV fluorescence. Solid residue was analysed by elementary analysis.

References :

- [1] J. Agric. Food Chem. 2000, 48, 817 – 824.
- [2] JAAP, 95, 112-114, 2012
- [3] J. Braz. Chem. Soc., 11(5), 491-494, 2000
- [4] ChemSusChem. 2020, 13 (17), 4633-4648



Keywords : Kinetic modeling, solvation properties, equation of state

General context, scientific issues :

Automatic kinetic mechanism generators used in detailed kinetic modeling enable an accurate prediction of the evolution of ideal gas oxidation processes. Reliable thermodynamic models are then required to adapt such generators for oxidation reactions taking place in liquids or supercritical fluids.

Objectives and stakes :

The main goal is to propose a flexible framework to describe oxidation processes taking place in liquid or supercritical solvents. It is assumed that the kinetic mechanisms are the same in the solvent or in the ideal gas phase but that kinetic constant must be corrected. The role of the corrections is to incorporate solvation effects into the kinetic model. These effects arise from the molecular interactions established between solutes (molecules and free radicals) and solvents [1].

Methodology :

The aforementioned corrections are based on the solvation free energy ($\Delta_{solv}\bar{g}_i$) of the solutes in the bulk phase. For a given temperature (T), pressure (P) and composition (\mathbf{Z}), $\Delta_{solv}\bar{g}_i$ can be calculated as follows:

$$\Delta_{solv}\bar{g}_i(T, P, \mathbf{z}) = RT \ln \left[\frac{P \cdot V(T, P, \mathbf{z}) \cdot \phi_i(T, P, \mathbf{z})}{RT} \right]$$

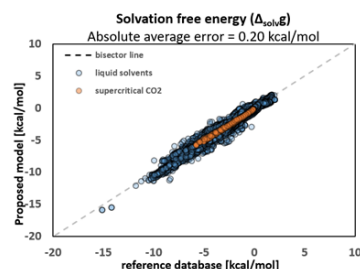
This approach relies on the calculation of the fugacity coefficient of solute molecules (ϕ_i), along with the estimation of the molar volume of the bulk phase (V). Both can be straightforwardly estimated by a cubic EoS. In this study, the tc-PR EoS (translated-consistent Peng-Robinson) was used [2]:

$$P = \frac{RT}{(V + c_i - b_i)} - \frac{a_i(T)}{(V + c_i)(V + c_i + b_i) + b(V + c_i - b_i)}$$

The attractive parameter (a_i), the co-volume (b_i), and the volume translation (c_i), are calculated based on the preliminary knowledge of the critical temperature ($T_{c,i}$), critical pressure ($P_{c,i}$) and acentric factor (ω_i) of molecules, or by a group contribution method developed in this work. This group-contribution method is essential for radical species for which ($T_{c,i}$, $P_{c,i}$ and ω_i) are not accessible experimentally.

The extension of tc-PR EoS to mixtures was done using an advanced mixing rule, which couples the EoS with an activity coefficient model [3]. A quantum-based activity coefficient model, called COSMO-RS [4] (short for *Conductor like Screening Model for Real Solvents*), was chosen to calculate the activity coefficients.

Illustration : Parity plot for the solvation free energy of molecular species and free radicals in liquid solvents and supercritical CO₂: comparison between experimental (reference) data and calculated data obtained by applying the EoS model developed in this thesis.



Main results



A good agreement between experimental and calculated data was obtained for the solvation free energy of molecular species and free radicals in liquid solvents, since the average deviation (AAD) was close to 0.2 kcal/mol.

It was found that alkyl radicals (primary, secondary, tertiary, vinylic, acetylenic, benzyl, and phenyl) have a solvation energy very close to that obtained for their parent molecules (H-atom added to the radical site). However, the same was not observed for carbonyl, alkoxy and peroxy radicals, due to changes in the association behavior, i.e., the ability to form hydrogen bonds.

Regarding the application of the tc-PR/COSMO-RS EoS in the supercritical domain, very reliable results were obtained for mixtures in which supercritical carbon dioxide is the solvent. The average absolute deviation obtained in such a case was only 0.11 kcal/mol. It was found that, for supercritical solvents, $\Delta_{solv}\bar{g}_i$ becomes pressure dependent, and the equation of state is the only high-throughput approach available in the literature that is capable of describe such a dependence.

References :

- [1] A. Jalan, R.H. West, W.H. Green, J. Phys. Chem. B. 117 (2013) 2955–2970.
- [2] Y. Le Guennec, R. Privat, J.-N. Jaubert, Fluid Phase Equilibria. 429 (2016) 301–312.
- [3] A. Pina-Martinez et al., Ind. Eng. Chem. Res. 60 (2021) 17228–17247.
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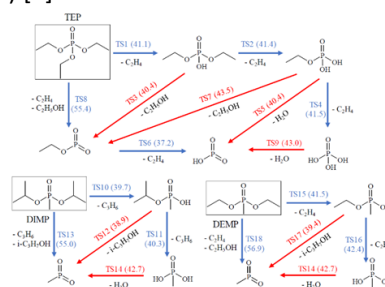
 <p>2023</p>	<p>Research subject: The thermodynamic and kinetic study of pyrolysis and combustion of organophosphorus compounds, and the provision of methods and models</p> <p>Vishal Kumar Porwal (post-doctoral researcher)</p> <p>Pr. René Fournet, Dr. Pierre-Alexandre Glaude, and Dr. Baptiste Sirjean</p> <p>Axe CiTherE, DGA</p>	
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Keywords : Thermodynamics, Kinetics, Pyrolysis, Combustion, Organophosphorus compounds, Modeling

General context, scientific issues :

The development of the most exhaustive possible models of the kinetics of thermal degradation by pyrolysis and combustion is essential in the context of risk assessment via the simulation tools of DGA Maîtrise NRBC. These models and data are used for understanding and predicting the vulnerability of organophosphorus compounds. They are intended to be injected into kinetic modeling codes, in particular, the Chemkin[1] and Cantera[2] software, modeling the fate of gas-phase reactants subjected to temperature and pressure stress.

Illustration : Molecular decomposition of sarin simulants (TEP, DIMP, and DEMP), showing six-centered (blue) and four-centered (red) pericyclic reactions with their respective energy (in kcal mol⁻¹).[3]



Objectives and stakes :

The study is divided into three parts. The first part of the study will focus on the implementation of the methodology developed previously by Lizardo-Huerta et al for three specific organophosphorus compounds.[3] The second part of the study will relate to the upgrading of the base of reactions of phosphorus-containing molecules of small size (POxHy). The third part of the study will focus on the determination of thermodynamic properties in the liquid phase.

Methodology :

We will first perform the benchmarking using the ab-initio computational methods from previously known studies on the organophosphorus molecules and select the one closest to the experimental values and computationally inexpensive. The geometry optimization and frequency calculations of small phosphorus-containing model molecules (e.g. P₂, PO, HPO, etc.) will be performed using computationally cheap but reasonable methods and then the gas phase enthalpy of formation (ΔH_f) will be calculated using the higher level theories using the methods used by Klippenstein et al.[4]

We will estimate the Bond dissociation energies (BDE) using the theory and basis set obtained from the aforementioned step to guide the construction of the combustion mechanism and to estimate the rate constants for each reaction pathway. Using the developed mechanism, we will then perform the kinetic and analytical simulations at high temperature and pressure using the Chemkin[1] package to draw the decomposition pathways of the target molecule (an example is depicted in the figure). The same steps will be repeated for the organophosphorus molecules in the liquid medium to complete the database.

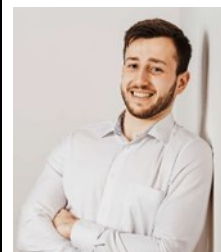
Main results

According to the available database, these types of molecules tend to decompose via radical reactions at high temperatures (>800K) and pressures (>5 bar).[3] One aspect that we will consider is the pericyclic reactions which also tend to compete with the radical reactions under the same conditions. The estimation of BDE and rate constants with higher accuracy ab-initio calculations will allow us to presume the scenarios where we could distinguish between the mechanisms of concerted pericyclic reaction followed by the decomposition or radical dissociation into simple molecules. [4]

Once the mechanism is estimated, we would also be able to predict the reaction path of similar species in the given conditions. By utilizing the most modern ab-initio methods, we will be able to update the database of the basic molecules obtained after the decomposition. Considering the toxicity of some of the organophosphorus molecules, with the updated database and the mechanisms we will be able to predict the various stages of the decomposition of a target molecule by simply detecting the decomposed species

References :

1. R. J. Kee, F. M. Rupley and J. A. Miller, Chemkin-II: A Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics, Sandia National Lab. (SNL-CA), Livermore, CA (United States), 1989.
2. Goodwin, David G, Moffat, Harry K, Schoegl, Ingmar, Speth, Raymond L and Weber, Bryan W, Cantera: An Object-oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes, Zenodo, 2022.
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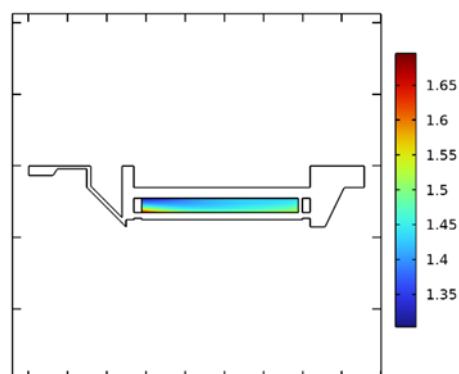


Keywords : r-CVI, modeling, pyrocarbone, C/C material

General context, scientific issues :

MBDA is seeking to develop knowledge and skills on the rapid chemical vapor infiltration process, based on the cracking of a hydrocarbon at constant temperature and pressure and with short residence time. This process allows densifying a fibrous preform by depositing carbon in order to create a high-performance material.

Illustration : Density of the preform after densification



Objectives and stakes :

The aim of this study is first to understand the chemistry and physico-chemical phenomena that occur during densification. Thanks to this, the goal will then be to develop a predictive model of the process in order to choose optimal parameters for densification. Another goal could be to propose designs of tooling parts to improve the properties of the final material. The stake of this work is to understand and improve the r-CVI process.

Main results

The graph above shows the density variation of the preform after the r-CVI cycle. It is possible to see a more important densification on the bottom surface thanks to higher temperature. The upper surface is less densified because of important thermal gradients in the tooling. It is possible to see that the interior of the preform is quite well densified, which indicates that the species are diffusing well.

More globally, the simulation results show the important impact of the temperature (and of the temperature gradients) on the densification and also highlighted the differences of velocities in the internal and external walls of the preform to be densified.

Methodology :

For the project, the experimental part and the development of the model will be done jointly. The experimental data produced by the company will initially be used to supply the model to adjust the various parameters and to make the modeling representative of experimental results. In a second time, the model will be used to predict the experiments and finally to define optimized process parameter for given densification objectives.

The model will be composed of 3 parts: a description of the flow, a description of the thermal exchanges and a description of the chemistry involved during the process. The flow will be governed by the Navier-Stokes equations in the empty parts of the tooling and by the Brinkmann equations in the porous part to be densified. The energy balances will be simulated using conduction and convection equations. The chemistry will be adapted from the research of Rémy Lacroix and Isabelle Ziegler on the mechanisms of pyrolysis and deposition from propane. [1-2]

References :

- [1] R. Lacroix, « Mécanisme cinétique hétérogène détaillé de dépôt de pyrocarbone », PhD Thesis, 2009.
- [2] I. Ziegler, « Modélisation cinétique des dépôts de pyrocarbone obtenus par pyrolyse d'hydrocarbures », 2004.



Keywords : Jet fuel combustion, combustion mechanism, scramjet fuel, jet fuel pyrolysis, jet fuel oxidation, kinetic modelling, detailed mechanism generation.

General context, scientific issues :

Active cooling is used on highly thermally loaded structures such as liquid rocket engine (1) or high speed ramjet (2). When the coolant is a hydrocarbon fuel, its heating may lead to pyrolysis. The development of detailed pyrolysis mechanisms for high-density jet fuels is therefore a principal issue.

Objectives and stakes :

In this thesis, the main goal is to understand the combustion behavior of a fuel called "D fuel." To achieve this goal, a detailed kinetic mechanism for both pyrolysis and oxidation of this fuel will be developed using ab initio quantum calculations and density function theory. This mechanism will be validated against experimental results obtained in a perfectly stirred reactor during the PhD or from literature review.

Methodology :

This work consists of 3 parts: determination of the fuel composition, experimental study of the pyrolysis and combustion of the fuel, generation of a reaction mechanism and simulations to validate it from experimental results.

1. Determination of the fuel composition:

The qualitative part of the composition determination is made by GC-MS. Then, 5 internal standards are injected with the pure fuel to quantify the proportion of each compound of the fuel using the De Saint Laumer (3) method to conclude on an exact composition.

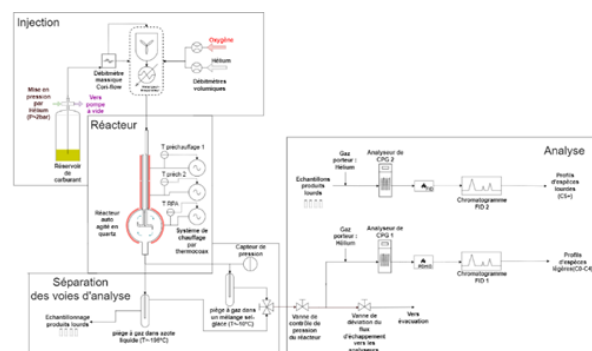
2. Experiments:

For this, an experimental pilot (see illustration) was set up to be able to make oxidation and pyrolysis between 600°C and 1000°C (depending on the studied compound), a residence time ranging from 0.5s to 4s and an equivalence ratio between 0.7 and 1.3. The products formed will be analyzed and quantified by gas chromatography.

3. Generation of the combustion mechanism:

Once the composition of the fuel is figured out, a kinetic mechanism will be developed to model the combustion and pyrolysis of this fuel. The kinetic constants and thermodynamic data will be obtained either by electronic structure calculations or by structure-reactivity correlations. A second part will consist in validating the model by comparison with the experimental data and to complete or change the mechanism accordingly. Once the mechanism is generated, it will be possible to use it for different operating conditions closer to those met in hypersonic vehicles.

Illustration : description of the experimental setup





Main results

The kinetic mechanism for a first molecule (Cumene) has been generated using quantum calculations with Gaussian 09® Rev. D.01 (4). This mechanism has been simulated using Chemkin Pro(5) and compared to experimental results obtained in a perfectly stirred reactor (see illustration above). The experimental conditions are: temperature between 863K and 1043K, 1s residence time, 800 Torr and for a molar composition of 1% of Cumene and 99% of Helium. A comparison of the experimental and simulated exhaust species profile has been made and a good agreement was obtained for primary products. Some differences have been noticed for few molecules (toluene, propadiene for example) or at elevated temperature. New reactions paths need to be added to the mechanism to fix these issues.

References :

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	<p align="center">Research subject: Development of thermodynamic model, algorithms and computational tools to assess the energy transformations of reactive working fluids in thermodynamic cycles</p> <p align="center">Konstantin Samukov (2nd year)</p> <p align="center">Romain Privat, Silvia Lasala</p> <p align="center">CITHERE</p>	
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Keywords : Reactive fluids, thermodynamics, thermal energy conversion

General context, scientific issues :

Conventional thermal engines and heat pumps are based on the use of thermodynamic cycles, which reveal strong performance limitations. The efficiency of these systems may be highly increased with use of a reactive working fluid, instead of a conventional inert fluid [1].

Objectives and stakes :

The main objective of the thesis is to develop a model for the thermodynamic description of the reactive fluids involved in reactive cycles and then, to develop a computational tool for the prediction of the thermodynamic properties of inert and reactive mixtures.

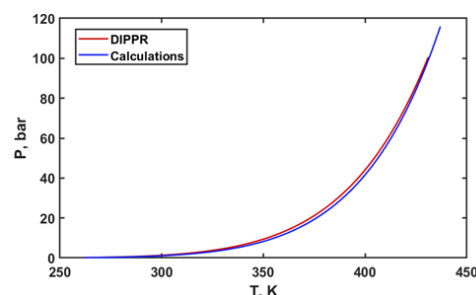
Methodology :

The model for the description of reactive fluids is based on a cubic equation of state (EoS) with appropriate mixing rules. The pure-component input properties of the cubic EoS which are the critical temperature T_c , critical pressure P_c and acentric factor ω , of each reacting compound are determined from the properties of reactive mixture. Calculation tool is entirely coded in Fortran, and requires the preliminary selection, improvement and implementation of: (1) a predictive equation of state; (2) algorithms for chemical equilibrium calculations in the presence of chemical reactions and multiple fluid phases. The developed calculation program will be used in the project to model reactive power cycles involving real fluids (i.e., fluids described with a cubic EoS: a model for real fluids), in the framework of the ERC project « REACHER » [2]. Various reactive fluids will be considered in order to identify the ones leading to the highest cycle performance indices (efficiency, compactness ...). As a parallel activity, this thesis is contributing to the understanding of the researches performed on the subject of reactive fluids in power cycles in the Soviet Union.

References :

- [1] S. Lasala, R. Privat, O. Herbinet, P. Arpentiner, D. Bonalumi, and J.-N. Jaubert. *Energy Convers. Manag.* 2021: 113685.
- [2] Website of the project REACHER: <https://www.univ-lorraine.fr/erc-reacher/>
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Illustration : VLE pressure in the reactive N_2O_4 - NO_2 system. The "DIPPR" curve is a simple correlation of experimental data and can be considered as an experimental information. The curve "Calculations" is computed from the Peng-Robinson EoS with advanced mixing rules.



Main results

As mentioned above, the Peng-Robinson equation of state combined with advanced mixing rules is chosen to describe the N_2O_4 - NO_2 system. The considered mixing rules involve the residual part of an activity coefficient model which is here assumed to be null (it means that molecules of the reactive mixture exhibit the same interactions). The EoS input properties of pure compounds, that are the critical properties T_c , P_c and the acentric factors of pure N_2O_4 and NO_2 have been estimated by using different techniques and in particular: molecular Monte Carlo simulations.

Regarding chemical equilibrium calculations, different strategies have been developed:

for reacting mixtures made up of binary systems A_2/A (linked by the balanced chemical equation $A_2 = 2A$) calculations of chemical equilibria in single phases were performed by solving the condition for chemical equilibria at given temperature and pressure. Calculations of VLE for reacting binary systems are based on finding a solution of the system of equations: for a given value of temperature, the system of equations describing properties of the phases, phase and chemical equilibria are solved for pressure, molar volumes and molar compositions of the phases. Calculated pressures were compared to the experimental values. The coordinates of the unique critical point of the reacting system were calculated by a modification of an algorithm proposed for non-reactive systems [3]. Finally, thermodynamic properties of the N_2O_4 - NO_2 system were calculated in a wide range of temperatures and pressures.

For reacting mixtures made up of p -component mixtures (with $p > 2$), RAND method [4] for single-phase and two-phase systems was implemented. It will be used for describing ternary mixtures involving a reacting binary fluid (A_2 , A) and an inert compound (CO_2 , for example). Such a ternary system could show interesting properties for reacting power cycles. This will be investigated in the framework of the present thesis.



Keywords : ozone-initiated oxidation, jet-stirred reactor, kinetic modeling, gas chromatography, synchrotron-based photoelectron spectroscopy

General context, scientific issues :

Ozone (O_3) addition is one of the promising methods to achieve improvement and control of combustion/ignition processes. However, the complexity of the chemistry induced by the ozonolysis reaction makes investigations on O_3 -assisted oxidation with alkenes still scarce.

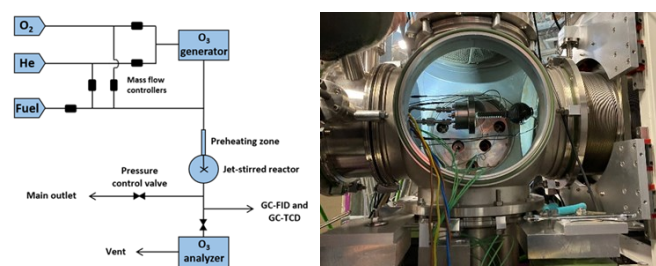
Objectives and stakes :

Experimental and kinetic modeling of the O_3 -initiated oxidation of 1-hexene in a jet-stirred reactor (JSR) through gas chromatography (GC) and photoelectron spectroscopy using a PEPICO spectrometer.

Methodology :

As an important component in gasoline surrogate fuels, in this work the oxidation of 1-hexene with (1000 ppm) and without O_3 was studied in a JSR from 350 to 800 K. The residence time, pressure, equivalence ratio, and initial mole fraction of 1-hexene were maintained at 2.5 s, 800 torr, 0.5, and 0.01, respectively. Quantification and identification of the main products and stable intermediates were performed in LRGP-Nancy by GC using a flame ionization detector (FID) coupled with mass spectrometry (MS). The experimental results were compared to an updated kinetic model of the literature by adding an O_3 sub-mechanism [1,2]. A complementary analysis for the identification intermediates was performed by coupling the JSR to synchrotron vacuum ultraviolet photoelectron photoion coincidence spectroscopy (SVUV-PEPICO) at Synchrotron SOLEIL.

Illustration : Scheme of the setup at LRGP (left) and photo of the JSR in the setup of Synchrotron SOLEIL (right)



Main results

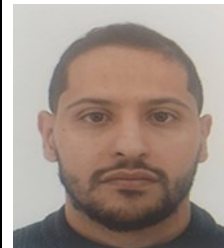
The addition of O_3 allowed the consumption of ~20% of 1-hexene from room temperature and maintained a significant conversion even in the negative temperature coefficient (NTC) area, even if no temperature shift of this region was noticed. Significant amounts of aldehydes and acids were quantified by GC, whereas spectroscopic analysis revealed the formation of ketohydroperoxides, which are well-known low-temperature combustion (LTC) branching agents. The kinetic model updated in this work based on ozonolysis global reactions predicts fairly well the mole fraction of the main products.

References :

- [1] Meng X. et al., Combust Flame 2017, 181 283–99.
- [2] Jian J. et al., Fuel 2022, 322 124–138.



PRODUCT ENGINEERING

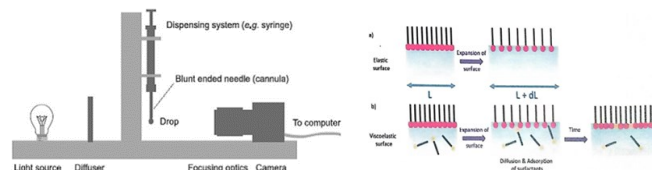


Keywords : Dilational viscoelasticity, Drop tensiometer, DWR, Interfacial rheology, Bulk rheology, L/Land L/G interfaces.

General context, scientific issues :

Interfaces between two immiscible liquids play a very important role since, numerous applications in daily life and industrial processes involve surface and interfacial properties, such as foods, medicine, detergents, etc. The interaction of molecules at the interface and interactions between interface and bulk influence the dynamic and static behavior of interfaces. So, is crucial to investigate the interfacial and volume properties that will have direct impact on the final product characteristics i.e., end-used properties.

Illustration : Scheme of the experimental set-up of dilational interfacial rheology at oil/water interface using drop tensiometer



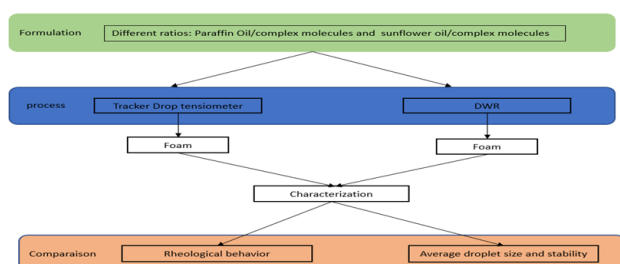
Main results

In our search we expect to obtain relations between results of the interfacial rheological study of oil/water stabilized by complex molecules performed by tracker drop tensiometer (dilational rheology) and by DWR (shear rheology) and similar study is conducted at gas/water interface. Also, we will be able to have clear idea about the link between bulk and interface properties. Moreover, this work will provide many information about the influences of interfacial rheology of these system on foam characterization and stability.

Objectives and stakes :

- Study and compare the interface rheology properties of L/L and L/G interfaces using drop tensiometer and double wall ring system.
- investigate the link between the results obtained in bulk and interface.
- Probe the impact of the interfacial rheology properties on the foam stability.

Methodology :



References :

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<p>2023</p> 	<p>Research subject: Modeling and development of an innovative medical device to test anti-cancer drugs</p> <p>Cyprien Berthelemy (1st year)</p> <p>Halima Alem Marchand, Cécile Lemaître, Rainier Hriez</p> <p>Institut Jean Lamour, LRGP</p>	
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Keywords : Modeling, Microfluidics, Organ-on-a-chip, Cancer therapy, Medical Devices

General context, scientific issues :

Despite the promising efficacy shown by some nanoparticles (NPs) in preclinical studies, less than 5% of anticancer nanomedicine that reach Phase I get an EU approval which make oncology the pharmaceutical domain with the lowest rate of success [1]. The cause of this 95% failure rate of the drugs from Phase I to Authority approval submission is related to the low efficacy and safety (56 and 28% failure respectively) which is essentially due to the difficulty of establishing correlation between nanosystems' efficacy and toxicity across species to be translated to human [2].

Illustration : No Illustration due to confidentiality

Objectives and stakes :

•To address this issue, new pre-clinical models are developed based on 3D cell cultures in dynamic conditions. They can be called organ-on-chip [3]. My PhD project is to design and develop a device that combines microfluidic and cell culture to provide an advanced tool for anticancer drug test and their further development

Main results

Since the beginning of my PhD, I have performed a significative amount of different numerical simulations, with the CFD software ANSYS Fluent, that model a microfluidic chip composed of a distributor of 2 inlets, one for pure solvent and the other one for drug-loaded solvent, and 5 outlets, feeding 5 culture chambers designed to house cancer cells. The 5 chambers are supplied with 5 different concentrations of drug (0%, 25%, 50%, 75%, 100% of the injected drug concentration), which will allow to determine a toxicity threshold concentration for the cells. The best design predicted by the simulations was then manufactured in the laboratory and is currently tested.

The next step of my PhD program is to conduct experiments to validate the theoretical calculations.



The second step will be to add a layer of endothelial cells on the channels walls and to feed the system with blood, in order to approach better the in vivo conditions

Methodology :

The objective of this thesis is to use a dual numerical and experimental approach. It combines the recognized skills in microfluidics and numerical fluid mechanics of the LRGP, and the skills in materials science and 3D bioprinting of the IJL. This project is the continuation of anterior work that has led to the current drafting of a patent combining the know-how of the two laboratories. The idea is to improve the current model and develop a smaller one that enables in one chip to test different concentrations. First, by doing numerical simulation with the software ANSYS Fluent and then producing a prototype to validate the simulation. The validation will be done by testing the prototype with Doxorubicine (anti-cancer drug) as its chemical properties are well known. When the prototype is validated, the model will be complexified (by for example seeding cells in the Biochip or changing the nature of the media in the chip) and we will continue to go back and forth between simulation and experiments. If a point is reached where the complexity of the model is deemed sufficient, it will be used to test different drugs and to understand how they behave in the model.

References :

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<p>2023</p> 	<p>Research subject: Green process for valorization of bioplastics: enzymatic transesterification of polylactic acid</p> <p>Alaric Catard (2nd year)</p> <p>Sandrine Hoppe, Isabelle Chevalot</p> <p>Génie des Produits</p>	
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Keywords : polylactic acid, enzymes, green solvents, hydrolysis, Novozyme 435®, PLAase III, transesterification

General context, scientific issues :

Last decades have seen the emergence of biobased plastics, such as polylactide (PLA) to decrease the environmental impacts of plastics. However, the limited ability of PLA to biodegrade and the absence of recycling industries for it makes necessary the development of recycling processes.

Objectives and stakes :

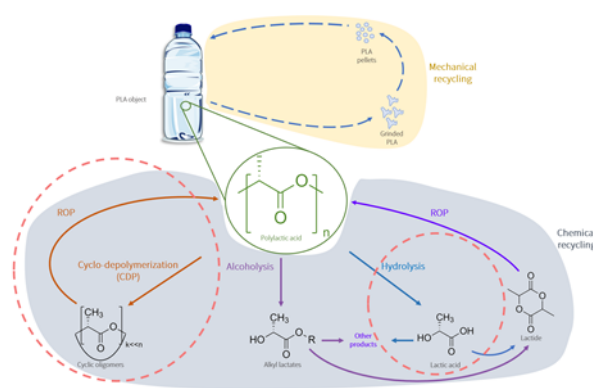
This work aims to explore two ways of enzymatic recycling of end-life PLA in a sustainable way: transesterification and hydrolysis. The first one is based on the use of the immobilized lipase B of *C. antarctica* (Novozyme 435®) using sustainable solvents and high temperatures to get cyclic repolymerizable oligomers. The second one relies on the heterologous expression in *E. coli* of a protease from *A. orientalis* and its use in hydrolysis of poly(L-lactide) to obtain lactic acid.

Methodology :

Concerning the enzymatic transesterification of PLA, it was necessary to check different points before setting up the depolymerization of PLA: (1) the solubility of PLA into green solvents (Dimethyl carbonate (DMC) and diethyl carbonate (DEC)), (2) the residual activity of the enzyme after different times at high temperatures in these solvents, (3) the stability of the solvents after incubation at high temperature with the enzyme. After that, the enzymatic depolymerization have been carried out and the size of the products have been analyzed using size exclusion chromatography.

For the enzymatic hydrolysis approach, the protease (PLAase III) had to be characterized with bioinformatic tools. Then, the heterologous expression has been performed using different plasmids to enable the successful expression of the enzyme into an active state. Presence and identification of the active state of the enzyme have been managed thanks to SDS-PAGE electrophoresis. Moreover, the hydrolysis ability against esters and proteins of the enzyme have been studied. Finally, the ability of PLAase III to hydrolyze PLLA into lactic acid will be performed and analyzed using high performance liquid chromatography

Illustration : Schematic representation of the different recycling ways of PLA. Circled in red: the two approaches explored during this PhD thesis.





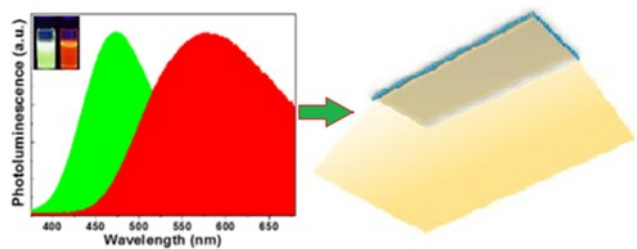
Main results

It has been shown that PLA is soluble in DMC and DEC at high temperatures: 115 g.L⁻¹ in DEC and 120 g.L⁻¹. Moreover, the immobilized enzyme keeps a significant activity at high temperatures: 25% at 110°C after 48h and 30% after 24h at 120°C in DEC. Also, the solvents are quite stable after incubation with the enzyme with few amounts of their hydrolysis products. Hydrolysis reactions could have been catalyzed by the enzyme thanks to the residual moisture. Depolymerization reactions are still tested to enable depolymerization of PLA into cyclic oligomers by intra-transesterification reactions (1,2).

Bioinformatic analysis of the PLAase III showed that it is composed of 3 parts: a signal peptide, a pro-region to enable folding of the third part, the catalytic region. Works are in progress on heterologous expression of PLAase III and successful expression of the full enzyme (pro and catalytic regions) in small volumes has been achieved. However, the confirmation of the presence of the mature catalytic region has to be demonstrated.

References :

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<p>2023</p> 	<p>Research subject: Photoluminescent textiles incorporating QDs/photopolymer composites: towards a new generation of lighting devices</p> <p>Bilel CHOUCHE (research engineer)</p> <p>Raphaël SCHNEIDER</p> <p>Génie des Produits</p>	
<p>Keywords : Quantum dots (QDs), CuInS₂/ZnS, AgInS₂/ZnS, Photoluminescence, QDs/photopolymer composites, lighting devices</p>		
<p>General context, scientific issues :</p> <p>Luminescent nanoparticles (NPs) have been widely used in research and application fields, especially for the development of light-emitting diodes (LEDs) [1,2]. Quantum dots (QDs) are promising materials for the emissive component of LEDs due to their high colour saturation in a narrow wavelength range, easy colour tunability by control of their size and/or composition, and prominent stability. In this context, our work is based on the development of a new generation of QDs with exceptional characteristics for LEDs applications.</p>	<p>Illustration : PL emission spectra of green and red QDs (at left) and schematic illustration of lighting ceilings and the chromatic analysis (at right)</p> 	
<p>Objectives and stakes :</p> <p>The overall objective of this work is to develop innovative photoluminescent textiles by coating them with an advanced composite film combining heavy metal-free and non-toxic QDs with a biocompatible formulation of light-cured methacrylate for a new generation of photoluminescent textiles.</p>	<p>Main results</p> <p>During the first half of work:</p> <p>Red, orange, yellow and green-emitting CuInS₂/ZnS, AgInS₂/ZnS and AgCuInS₂/ZnS QDs were prepared via the thermal decomposition of organometallic precursors in organic phase.</p> <p>The crystal structure and phase purity of the as prepared QDs were analyzed via X-ray powder diffraction (XRD). The results revealed that the prepared particles crystallize in the tetragonal chalcopyrite phase (JCPDS 40-1488) [3].</p> <p>Transmission electron microscopy analysis shows spherical-shaped particles with average sizes in the order of 2.5 nm.</p> <p>The prepared particles show high photoluminescence properties with quantum yields varying between 40 and 80%.</p> <p>Photostability tests of the synthesized QDs have been carried out and show that they are photostable under LED irradiation at 405 nm.</p>	
<p>Methodology :</p> <p>To achieve the objective previously described, the following methodology will be implemented:</p> <ol style="list-style-type: none"> 1- Synthesis of silver- or copper-based QDs with tunable optical properties in the visible range. 2- Structural and optical characterizations of synthesized QDs, and study of their photostability. 3- Developing a photo-induced synthesis of highly photoluminescent QDs/polymer nanoassemblies by adjusting the size, composition, organization/spatial distribution of QDs in the polymer film and implementing this technology in textile applications. 4- Preparing new photoluminescent textiles with targeted photometric characteristics when combined with violet/blue LEDs chips. 	<p>References :</p> <ol style="list-style-type: none"> [1] X. Wang, X. Yan, W. Li, K. Sun, Adv. Mater. 24 (2012) 2742–2747. [2] Z. Xia, C. Ma, M.S. Molokeev, Q. Liu, K. Rickert, K.R. Poeppelmeier, J. Am. Chem. Soc. 137 (2015) 12494–12497. [3] Zhe Hu, Hanxu Lu, Wenjie Zhou, Jinxin Wei, Hanqing Dai, Hong Liu, Zhiyong Xiong, Fengxian Xie, Wanlu Zhang, Ruiqi-an Guo, J. Mater. Sci. Technol. 134 (2023) 189. 	



Keywords : Antioxidant activity, phenolic compounds, *D. glomerata*, functionalization, antioxidant quantum dots.

General context, scientific issues :

A lot of attention is being paid to carbon derived nanoparticles. Carbon derived nanomaterials including CQDs are semiconductors with potential applications in several fields [1]. CQDs are produced from plant and are environmentally friendly [2] and have antioxidant activity [3].

Objectives and stakes :

Produce CQDs with high antioxidant activity using *D. glomerata* pods as biomass.

Evaluate different processes allowing to produce CQDs exhibiting both high fluorescence quantum yields and high antioxidant activity.

Determine some area of applications of the so-produced CQDs.

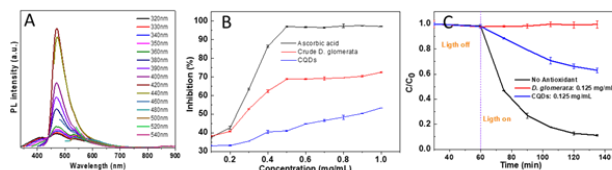
Methodology :

CQDs were produced by a hydrothermal method in basic medium [4].

CQDs were purified by dialysis [5], and characterized by spectroscopic methods (UV-visible absorption and fluorescence spectra) and X-ray diffraction (XRD).

The antioxidant properties of CQDs were evaluated (radical scavenging activity, reducing properties,...).

Illustration : (A) Fluorescence spectra when varying the excitation wavelength and (B,C) antioxidant properties of CQDs.



Main results

Fig. A shows that CQDs produced from *D. glomerata* pods are fluorescent and that the emission depends on the excitation wavelength. Thus, CQDs can be used as fluorescent nanoprobes for cellular imaging and sensing [6]



CQDs exhibit reducing properties as well as the crude extract used for their production. Fig. B shows that the extract and CQDs can reduce potassium permanganate (ascorbic acid was used as reference).

Fig. C shows that CQDs can also scavenge prooxidants (superoxide and hydroxyl radicals, hydrogen peroxide,..., generated by the graphitic carbon nitride photocatalyst. The presence of CQDs inhibited the degradation of a dye by ca. 60%, while the inhibition is total using the crude extract. The antioxidant property of the CQDs could be exploited to scavenge reactive oxygen species in cells [6]. CQDs have also been experimented in agriculture as antioxidant to improve plant growth and yield, which cannot directly be provided by the crude extract of biomass that is not easily assimilated by plants [7].

Our first results show that CQDs produced from *D. glomerata* pods could be valued for their antioxidant properties in pharmacy and food industries for the production of packing

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<p>2023</p> 	<p>Research subject: Elaboration and Design of New Hybrid Materials of MOF type with Advanced Functionalities for Photocatalysis Applied to Water Treatment</p> <p>Ola HAIDAR (2nd year)</p> <p>Thibault ROQUES-CARMES, Joumana TOUFAILY, Mohamad HMADEH.</p> <p>Génie des Produits, LEADDER-Lebanon, AUB-Lebanon.</p>	
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Keywords : Adsorption, Photocatalytic degradation, Emerging contaminants, Metal organic frameworks, UiO-66

General context, scientific issues :

Emerging contaminants in water pose an increasing environmental concern, prompting the development of innovative materials and technologies for efficient removal[1]. Among these, metal-organic frameworks (MOFs) have emerged as promising materials for water remediation, offering ultrahigh porosity, high surface area, flexibility, chemical tunability, and excellent chemical and thermal stability[2].

Objectives and stakes :

The objective of this project is to utilize Zirconium-based MOFs, specifically UiO-66, as effective materials for the adsorption and photodegradation-based removal of emerging contaminants from water. To this end, various defective, functionalized, and doped UiO-66 derivatives will be synthesized by combining different type of modulators, organic linkers, and metal salt.

The resulting UiO-66 MOFs structures will be characterized using XRD, SEM/EDX, TGA, and BET techniques to determine their suitability for eliminating specific model pollutants.

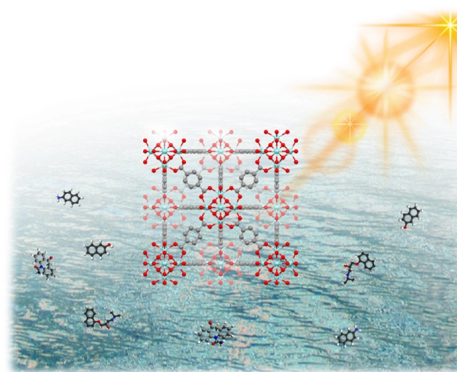
Methodology :

1. Synthesis and characterization of rigid UiO-66(Zr) structures.
2. Adsorption and photocatalytic degradation tests using model pollutants, including Carbamazepine, Ibuprofen, Metolachlor, Bisphenol A, Propranolol hydrochloride, 2-Naphthol, 1-Naphthyl amine, and 2,4-Dichlorophenol.
3. Evaluation of the effectiveness of MOF structures in removing a mixture of micropollutants from real water samples.

References :

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Illustration : Removal of ECs using MOFs.



Main results

Using solvothermal methods, we successfully synthesized a collection of Zr-based MOFs with defects, functionalization, and doping. These MOFs were extensively characterized using techniques such as X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), BET analysis, and thermogravimetric analysis (TGA). The introduction of defects in the UiO-66 MOFs was achieved through two methods: by incorporating a monocarboxylic acid modulator (acetic acid (AA) or trifluoroacetic acid (TFA)) during synthesis, as seen in UiO-66-(AA) and UiO-66-(TFA), or through thermal treatment using thermolabile ligands, resulting in hierarchically porous UiO-66, HP-UiO-66. These induced defects led to the formation of MOFs with distinct characteristics and increased porosity.

To obtain functionalized UiO-66, we utilized a ligand containing functional groups such as NH₂, OH and SH. This led to the synthesis of UiO-66(NH₂) and UiO-66(OH)₂, where the functional groups were incorporated into the MOF structure.

By introducing different metal salts during the synthesis process, we successfully obtained doped UiO-66 structures. These doped MOFs contained two different metal ions, including Ti, Ce, Co, Fe, and Nb, incorporated into zirconium cluster.

The comprehensive characterization allowed us to identify optimal functional groups, levels of defects, and metal combinations that enhance the adsorptive and catalytic properties of MOFs. Based on these findings, we selected the most effective MOF for further adsorption and photodegradation tests for 1-Naphthylamine (1-NA).

The defected series of UiO-66, namely HP-UiO-66, UiO-66-(AA), and UiO-66 (TFA). was used for the removal of 1-NA, and demonstrated significantly higher adsorption capacities reaching values of 550, 356, and 302 mg.g⁻¹, respectively.

The use of Fe-doped UiO-66 in a combined photocatalysis and advanced oxidation process with persulfate, exhibited remarkable efficiency in degrading 1-NA. After a duration of 30 minutes, the Fe-doped UiO-66 achieved complete degradation, reaching a degradation efficiency of 100%. This study will help us determine the best functional groups, level of defects, and metal combination to enhance MOF's adsorption and catalysis properties. It is anticipated that this work will pave the way for the development of new and highly efficient MOF for water remediation.



Keywords : Cu-doped ZnO nanorods , Composite materials, dye, photodeposition, photocatalysis.

General context, scientific issues :

Waste water containing hazardous organic pollutants from various industries causes severe environmental pollution. The organic dyes in the effluents coming from the industries are difficult to degrade due to their high stability. One of the drop priorities today is to find an efficient solution for environmental remediation [1]. Photocatalytic degradation of organic dyes and pollutants is one of the most efficient and cost efficient methods used for this purpose. Photocatalysis provides a promising technique for the removal of toxic organic pollutants from industrial waste water and may solve some of the major environmental issues originating from contaminated water [2].

Objectives and stakes :

Our objectives are:

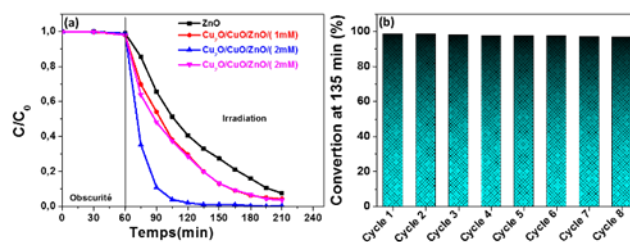
- (i) Design of new nanocomposites by functionalization of zinc oxide ZnO nanorods with Cu-based nanoparticles.
- (ii) Analyse the effect of processing parameters on the degradation of organic contaminants.
- (iii) Evaluate the performance of the new materials for photocatalytic water remediation under solar light irradiation.
- (iv) Study the effect of pollutant concentration, catalyst mass, light irradiance, pH and catalyst composition on the photocatalytic activity.
- (v) Evaluated the stability of the photocatalysts.

Methodology :

To perform the photodeposition of Cu nanoparticles onto ZnO, we used a Xe lamp to illuminate ZnO powder dispersed in an aqueous solution containing the Cu(II) precursor. Namely, 150 mg of ZnO rods synthesized by a solvothermal method were irradiated in the presence of a 2mM Cu(NO₃)₂ solution for a period of 5 h .The Cu/ZnO composite was collected by centrifugation and purified by washing before being dried in air overnight at 100°C [3].

The prepared materials were characterized by FTIR, SEM, TEM, BET, XRD, XPS, Raman spectroscopy and UV-visible absorption. The photocatalytic performance of pure ZnO and Cu₂O/CuO/ZnO catalysts was evaluated for the elimination of organic contaminants in water.

Illustration : (a) Effect of the Cu loading on the photocatalytic degradation of Naproxen (b) Recyclability of the Cu₂O/CuO/ZnO photocatalyst



Main results

- The Cu₂O/CuO/ZnO catalyst exhibits a significantly enhanced activity when compared to ZnO.
- Naproxen can be photodegraded by 97% in 60 min under solar irradiation using Cu₂O/CuO/ZnO (2 mM) (Figure 2a).
- The Cu₂O/CuO/ZnO catalysts shows a good stability (Figure 2b) and DRX analyses confirm that the crystallinity of the photocatalyst is not affected after 8 cycle re-uses.

References :

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Keywords : By-product valorization, antioxidant and anti-inflammatory bioactivity, polyphenols, ion exchange adsorption, membrane enzymatic reactors

General context, scientific issues :

The valorization of liquid effluents from rapeseed and sunflower-based protein production is a major socio-economic challenge. These effluents contain phenolic acid esters with beneficial properties for health, but their availability on the market is limited. A sustainable production of these molecules from the effluents would allow to meet the needs in phenolic acids and to valorize the effluents. [1][2]

Objectives and stakes :

The aim of this thesis project is to develop a process coupling adsorption, reaction and membrane separation for the continuous production of phenolic acids (sinapic acid) from phenolic esters (sinapine) present in industrial effluents from rapeseed and sunflower protein production. Coupling the enzymatic reaction to NF membranes would enable efficient separation of phenolic acids and enzymes, exploiting their differences in charge and molecular weight. This innovative approach will be based on experimental studies, as well as simulations, modeling and optimization.

Methodology :

The methodological work is divided into four distinct phases. Firstly, the influence of the conversion rate of sinapine hydrolysis on the biological properties of sinapine/sinapic acid mixtures was studied. This will enable us to define the target conversion rate for the reaction. Next, we will examine the adsorption/hydrolysis coupling process. In the first phase, we will study the adsorption of sinapine on a resin (screening, kinetics, adsorption isotherm) and the effect of reaction conditions (pH, T) on reaction kinetics. The third phase consists in modeling the influence of reaction conditions (pH, T, activity/substrate) on the kinetics of enzymatic hydrolysis of sinapine on the adsorbed resin (under the conditions chosen in the previous step). Finally, desorption will be studied. In the final phase, a study will be carried out to assess the impact of filtration conditions (TMP, pH, T) on the transfer of substrates (sinapine and chlorogenic acid) and products (sinapic acid and caffeic acid) through a selection of nanofiltration membranes. These phases will enable the selection of appropriate membranes and operating conditions for continuous reactor operation. Phenolic esters obtained from real discharges will be used in these studies. Finally, a system modeling and simulation approach will be developed to find the optimum conditions for continuous reactor operation, based on specific criteria such as bioactivity, enzymatic cost, productivity, yield and environmental impact.

Illustration : General strategy for the valorisation of the by-products of oilseed protein production



Main results

1. Screening of cation exchange resins and pH conditions for phenolic ester adsorption: Two resin-pH pairs were selected based on the following criteria: Higher adsorption rate and the stability of phenolic compounds. Further tests will determine the optimal resin between the two selected based on desorption rate and preservation of enzymatic activity.
2. Adsorption kinetics study: The equilibrium time for each resin was determined. In order to regress the results using linearized models, additional kinetics tests with more samples taken before reaching equilibrium will be conducted.
3. Identification of the optimal composition of enzymatic hydrolysis product based on the antioxidant activity of mixtures prepared with standards [3]: The antioxidant activity in the mixtures corresponds to the cumulative effects of each phenolic compound, depending on its concentration in the mixture. The maximum concentration of sinapic acid corresponds to the best antioxidant activity, making it suitable to target maximum conversion of the ester into phenolic acid through enzymatic hydrolysis.

References :

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Keywords : Bio-based itaconate elastomers, emulsion polymerization process, methacrylic acid, zinc oxide, crosslinking reaction, mechanical properties

General context, scientific issues :

Ionomers belong to a special category of polymers that contain a low level (<10%) of ionic functional groups (such as COO^- or SO_3^{2-}) in the hydrocarbon backbone. The presence of ionic moieties in organic polymers causes significant improvements to their physical and mechanical properties[1]. The carboxylated itaconate (PDBIBA) elastomer is an ionomer containing a carboxyl functional group, which is obtained by polymerizing dibutyl itaconate (DBI), butadiene (BD) and methacrylic acid (MAA). They bear both double bonds and carboxyl groups which are potentially reactive. Therefore, PDBIBA elastomers can achieve crosslinking not only through the double bonds using traditional crosslinking agents such as sulfur or peroxide, but also through ionic interactions between the carboxylic groups and metal oxides such as zinc oxide or magnesium oxide. For example, massive salt-bondings in polymerized Zn^{2+} or Mg^{2+} based unsaturated carboxylic acid salt molecules had strong electrostatic interaction, which could restrict the mobility of circumambient rubber chains. Simultaneously, the ion clusters yielded a high modulus because they functioned as effective reinforcing agent[2].

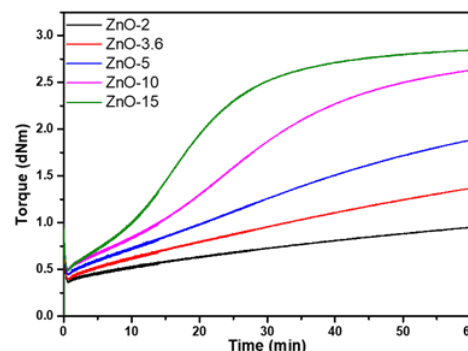
Objectives and stakes :

During the molding process of carboxylated itaconate elastomers in the presence of metal oxide, a carboxylic acid salt is formed that results in the formation of ionic elastomers or ionomers with greatly improved physical properties. The objective of this project is to cross-link carboxylated itaconate elastomers using zinc oxide, to analyze the reaction process of carboxylated itaconate elastomers with zinc oxide by means of vulcanization curves, FTIR and mechanical properties, and to investigate the effect of zinc oxide concentration and cross-linking temperature on the cross-linked carboxylated itaconate elastomers

Methodology :

Carboxylated itaconate elastomer contains 7.6 wt % carboxylic groups ($-\text{COOH}$). The vulcanization system is based on zinc oxide to create ionic cross-links. Compounds contain carboxylated itaconate elastomer and zinc oxide in which proportions of zinc oxide are 2, 3.6, 5, 10 and 15 phr, where 3.6 phr is the stoichiometric concentration to neutralize the carboxylic acid groups. The name of samples, e.g. ZnO-2, indicates the vulcanizing agent, ZnO and their amount (in phr). Compounds are prepared on a two-roll mill with a cylinder diameter of 15 cm and a length of 30 cm and a friction ratio of 1:1.2. The rolls are kept cold during the mixing procedure by circulating cold water through them. Vulcanization curves are obtained in a rotor-less rheometer.

Illustration : Elastic torque of PDBIBA with various concentrations of zinc oxide at 150 °C.



Main results



Table. Values of parameters that characterize the vulcanization curves at 150°C

Samples	Molar ratio (-COOH/ZnO)	T ₁₀ /min	T ₉₀ /min	M _H /(dN·m)	M _L /(dN·m)	M _H -M _L /(dN·m)	CRI
ZnO-2	1 : 0.28	1.6	52.1	1.0	0.4	0.6	1.98
ZnO-3.6	1 : 0.50	3.2	51.7	1.3	0.4	1.0	2.06
ZnO-5	1 : 0.69	4.2	51.0	1.8	0.4	1.4	2.14
ZnO-10	1 : 1.38	4.7	45.6	2.6	0.5	2.1	2.44
ZnO-15	1 : 2.08	4.9	33.8	2.8	0.5	2.3	3.46

Cross-linking of PDBIBA is confirmed by the elastic torque curves of the rheometer. The table shows the values of several parameters that characterize the vulcanization reaction of PDBIBA with various concentration of zinc oxide at 150°C. All the curves show the classical behavior of the vulcanization characteristics. In other words, when the sample is first added to the cavity of the rheometer, the viscosity decreases due to the increase of the sample temperature. Then the viscosity of the rubber increases sharply due to the cross-linking reaction, and the torque increases. With increasing reaction time, the sample torque tends to an equilibrium value again. Incorporation of zinc oxide brought a continuous increase in the elastic torque of PDBIBA, which confirms the occurrence of cross-linkings in the rubber matrix. As the concentration of ZnO increases, the maximum torque M_H increases, while the torque increment, $M_H - M_L$, rises gradually with the increase of ZnO content. This leads to an increase in crosslink density, which may improve the mechanical properties. Another point is the gradual increase of the cure index rate ($\text{CRI} = 100 / (T_{90} - T_{10})$), which indicates that as the ZnO content increases, the ZnO forms crosslinks with the carboxyl groups faster, due to the fact that the higher the concentration, the easier it is to access the carboxyl groups.

References :

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<p>2023</p> 	<p>Research subject: Advanced printable composites from MDF waste to furniture</p> <p>Johan RAMAUX (2nd year)</p> <p>Cécile NOUVEL, Isabelle ZIEGLER-DEVIN, Arnaud BESSERER</p> <p>Génie des Produits, Laboratoire d'Etude et Recherche sur le Matériau Bois (LERMAB), Acta Mobilier (Yonne, France)</p>	
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Keywords : 3D printing, Medium Density Fiberboard (MDF), Wood Composite, Recycling, Thermoplastic

General context, scientific issues :

Medium Density Fiberboard (MDF) is one of the most widely used materials for furniture. Every year, nearly 40 million m³ are wasted worldwide (1). Acta Mobilier produces large quantities of MDF waste as sawdust. Recycling MDF sawdust in 3D printing should allow the creation of unique products

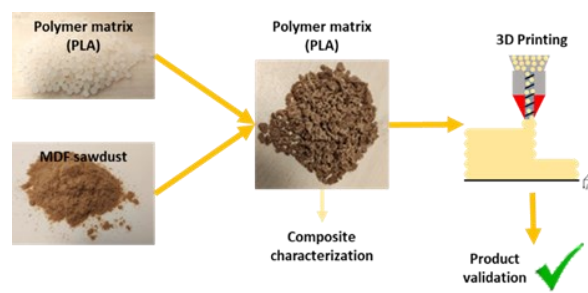
Objectives and stakes :

The general objective of this thesis is the production of a printable bio-based composite including MDF sawdust. The main challenges will be to re-use as much sawdust as possible in the printable composite material and to ensure its printability. To be presented as a new product, the material will have to comply with various European standards specific to furniture manufactured by Acta (cf. figure).

Methodology :

- 1/ Multi-modal characterization of the polylactic acid (PLA) and the MDF sawdust. The variability of sawdust mix is tightly correlated to the MDF suppliers and machining activities...
- 2/ Feasibility of the composite and printability and multi-modal characterization analysis.
- 3/ Optimization of the bio-composites formulation to meet the company's requirements and specifications. The printability of the composite will be evaluated by direct extrusion or through Fused Filament Fabrication (FFF) and its conformity to the various standards in force will be checked.

Illustration : Graphical abstract of the project

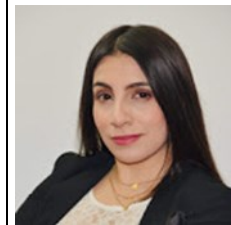


Main results

MDF sawdust and PLA have been characterized with various methods such like near infrared spectroscopy and microscopy. The mix between the PLA matrix and the MDF have been tested with different loadings rates. The composite obtained has been characterized with different techniques. The Melt Flow Index (MFI) have been measured (190°C/2.16 kg) and compared with recommendations for fused filament fabrication (2) of 10 g/10min. For the composite tested, the MFI was higher than 10 g/10min. The information obtained by the measurement of MFI is related to the facility of the materials to be 3D printed. To explain the high value of MFI, the dispersion between PLA and MDF was investigated. Several microscopy technologies such SEM or fluorescence microscopy (FM) have been used. SEM microscopy shows a mix between PLA and MDF but also a huge quantity of voids. Presence of voids have been confirmed by RX tomography and FM. FM makes possible to highlight the dispersion of sawdust within PLA (3). Consequently, to improve interactions and provide better properties of the composite, the

References :

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Keywords : Circularity, Hydrometallurgy, Li-ion batteries, Lithium recovery, Carbonation

General context, scientific issues :

Lithium is utilized in several applications, mostly to power electromobility. Its increasing demand has led to a risky supply chain and high prices. Lithium recovery from second sources has been explored widely in the recent years. Hydrometallurgy has demonstrated to be an effective process to extract cobalt, copper, manganese, nickel and lately lithium from spent Li-ion batteries.

Objectives and stakes :

The objective of this work is to develop a precipitation process of lithium carbonate from spent Li-ion batteries, which respects the environment, consumes little energy and material, by maximizing the yield and purity of the product obtained. Furthermore, it is essential to understand the stages of mass transfer in the reaction, as well as to achieve the desired properties in the final product.

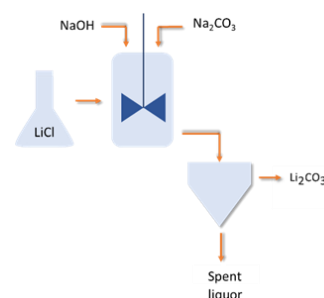
Methodology :

Lithium carbonate was obtained by chemical precipitation using sodium carbonate in a basic medium. Experiments were performed in a semi-open, thermostatically controlled and perfectly stirred reactor. Experimental conditions were varied, to make a quantitative and qualitative analysis of the final product. The contents of lithium were analyzed by inductively coupled plasma spectroscopy (ICP- iCap 6000). The filtered powder was morphological characterized by scanning electron microscopy (SEM Hitachi). Finally, the size distribution in mass and number was determined by laser granulometry (Mastersizer MS 3000).

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Illustration : Schematic drawing of the recovery of lithium carbonate from a lithium solution.



Main results

By varying the initial lithium concentration, it is observed variations in the yield, purity and cut off diameter. The higher lithium concentration higher yield is obtained, which agrees with the thermodynamic model simulated in PHREEQC (Fig.1). Granulometry results show that mean particle size becomes slightly smaller at higher concentrations (Fig.2). One possible explanation for this phenomenon is that, when a solution is more concentrated, the solute particles are more likely to come close to each other. This proximity leads nucleation mechanism to be more intense and originate smaller particles. In addition, a Kinetic approach using PHREEQC is envisaged.

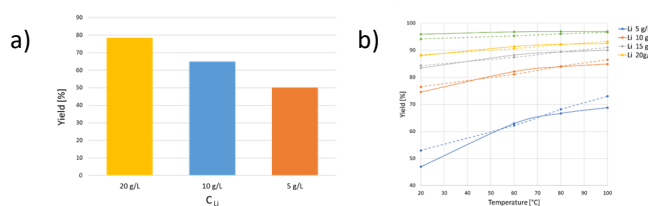


Figure 1. a) Yield results when varying lithium concentration b) Yield simulation at different lithium concentrations and temperatures. Dashed lines represent the yields manually computed.

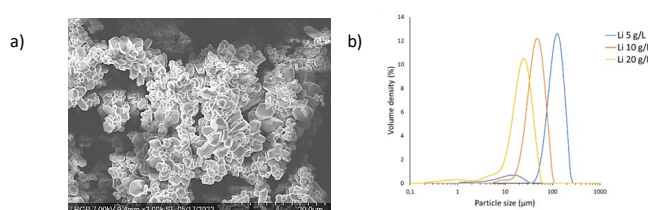
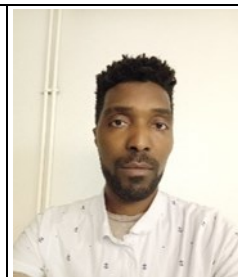


Figure 2. a) SEM image of Li_2CO_3 at an initial lithium concentration of 20 g/L. b) Particle size distribution of lithium carbonate at different initial lithium concentrations.



Keywords : Time-dependent fluids, Thixotropy, Viscoelasticity, Reactive fluids, Yield-stress fluids, Structural modeling, Numerical simulation.

General context, scientific issues :

Many industrial products (cosmetics, paints, food, etc.) exhibit time-dependent rheological behaviors such as viscoelasticity, chemical reaction and thixotropy. In order to manufacture correctly these products and to provide them the desired use properties, it is necessary to understand their rheological behavior. We are currently focusing on thixotropy. It is a time-dependent phenomenon manifested by a decrease in the viscosity of the material over time under constant stress. This phenomenon is often displayed by dispersions of particles or macromolecules within which weak interactions produce a structured three-dimensional network. Under the effect of stress, the network breaks, destructure occurs leading to facilitated flow of the fluid and therefore to a lower viscosity. This destructure is not instantaneous: it follows a kinetics often described by a first order differential equation, (Mewis et Wagner 2009). A rheological behavior model is associated with this structural kinetics, such as the Houska model (Houska 1981) for thixotropic yield stress fluids.

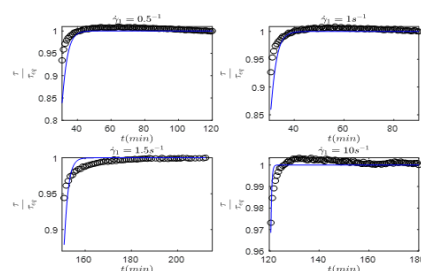
Objectives and stakes :

The rheological behavior of rheologically evolving fluids is the subject of numerous studies because knowledge of their flow modalities is necessary for the optimization of many industrial processes. However, structural modeling and numerical simulation of thixotropic fluids remains a subject in full development. The aim is first to propose a rheological model that describes thixotropy and secondly to couple this model with the conservation equations of mass and momentum in order to simulate the flow of these fluids. Computational fluid mechanics codes such as ANSYS Fluent software will be used.

Methodology :

During the present PhD, several thixotropic materials, commercial fluids and model fluids formulated in the laboratory, are currently being modeled. A model similar to those of Mewis and Houska is under development to describe the rheological behavior of these materials. The model parameters are determined from experiments carried out on rotary rheometers available at the LRP (a stress-controlled rheometer ARG2 and a strain-controlled rheometer ARES, both from TA Instruments).

Illustration : Normalized stress (stress divided by steady-state stress) against time at different shear-rate values. Experimental data are in black and model prediction in blue.



Main results

The proposed rheological model was adapted from Herschel-Bulkley model. In order to avoid numerical issues due to tending-to-infinity viscosity, the Herschel-Bulkley model was regularized. To capture the thixotropic effects, the consistency was modified to be a function of the time-dependent structure parameter that evolves according to Moore's kinetics. Hereafter the proposed model in a scalar form:



$$\begin{cases} \eta(\dot{\gamma}) = k(\lambda)\dot{\gamma}^{n-1} + \frac{\tau_y}{\dot{\gamma}} & \text{if } \dot{\gamma} \geq \dot{\gamma}_c \\ \eta(\dot{\gamma}) = \frac{\tau_y}{\dot{\gamma}_c} \left(2 - \frac{\dot{\gamma}}{\dot{\gamma}_c}\right) + k(\lambda)\dot{\gamma}_c^{n-1} \left((2-n) + (n-1)\frac{\dot{\gamma}}{\dot{\gamma}_c}\right) & \text{if } \dot{\gamma} < \dot{\gamma}_c \end{cases} \quad (1)$$

where λ is governed by Moore kinetics:

$$\frac{d\lambda}{dt} = -k_1\dot{\gamma}\lambda + k_2(1 - \lambda) \quad (2)$$

References :

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<p>2023</p> 	<p>Research subject: Recycling in short circuit of used plastic mixtures by additive manufacturing</p> <p>Benjamin Sandei (1st year)</p> <p>Cécile Nouvel, Valérie Massardier (IMP CNRS UMR 5223)</p> <p>LRGP-Axe Génie des Produits, Ingénierie des Matériaux Polymères (IMP) CNRS UMR 5223 Lyon</p>	
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Keywords : recycling, additive manufacturing, polymer, blend, post-consumer plastic, extrusion, circular economy

General context, scientific issues :

The plastic waste management has become a serious challenge on a global scale. Despite technical and legislative evolutions, multi-layered packaging or polymers mixtures difficult to sort by NIR are still difficult to recycle by direct mechanical recycling. One of the possible solutions consists in valorizing these non-recycled plastic waste streams in short circuits using 3D printing [1].

Objectives and stakes :

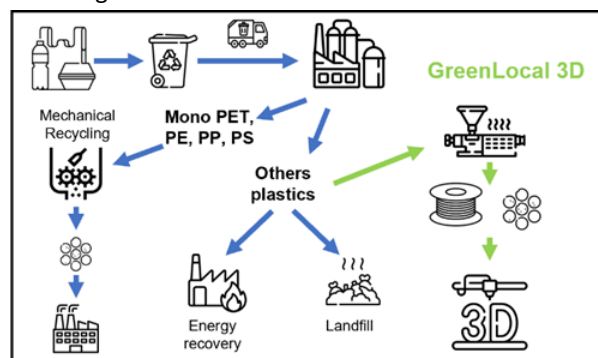
The PhD will contribute to the ANR (French National Agency for Research) "Global approach for the recycling in short circuit of used plastic by additive manufacturing". More specifically, this concerns the short-circuit valorization of post-consumer polymer wastes that is currently not recycled, such as Poly(ethylene terephthalate) (PET), Polyethylene (PE) and Polylactide (PLA), in particular when they are mixed, it is necessary to develop "formulation-processes" couples for their valorization.

Methodology :

After the choosing the mixtures to be studied, the first objective of this work will consist in compatibilizing virgin polymers representative of these streams, with the objective to design formulated "model" mixtures suitable for 3D printing. These blends will be produced by twin-screw extrusion. The rheological, thermal, mechanical and morphological properties of these materials will be characterized. The formulations giving the best results will be transposed to waste polymer mixtures. The systematic study of virgin and waste polymer blends will not only enable us to optimize the formulations and extrusion conditions but also to assess the robustness of the formulation with respect to the variability of the material streams coming from the sorting facilities. The robustness of the mix processing conditions will be validated by tests on equipment available in both laboratories, at different scales.

Finally, the materials obtained will be 3D printed, either in the form of granules (FGF) or in the form of filament (FFF). The properties of the parts produced will be measured and will allow the qualification of the recycled materials and their shaping process.

Illustration : Incorporation of GreenLocal 3D in the plastic waste management



Main results

First of all, a review on postconsumer plastics waste has been carried out to identify the polymers responding to project criteria. Multilayers PET/PE trays and the presence of PLA in PET streams look to be the most common issue encountered during mechanical recycling. A complementary survey will be realized by another PhD student of this project. Then, a bibliographic approach has been carried out regarding the miscibility of PE and PLA on PET blends. A list of potential compatibilizers has also been established. Copolymers including glycidyl methacrylate seem to be the most promising compatibilizers for PET blends [2]. The experimental part is first performed on virgin polymers representing plastic waste. Despite the presence of PLA in PET streams, both being polyesters, NIRS analysis (technology used in sorting centers) has shown that their spectra are sufficiently dissimilar to differentiate them. After characterizing each resin on its own, uncompatibilized PET/PE blends will be studied. A first analysis of their MFI showed a very important difference in their melt flow, which constitute a major challenge to produce blends [3]. The choice of the extruder will be made accordingly, before tackling the compatibility of these mixtures and the study of their properties.

References :

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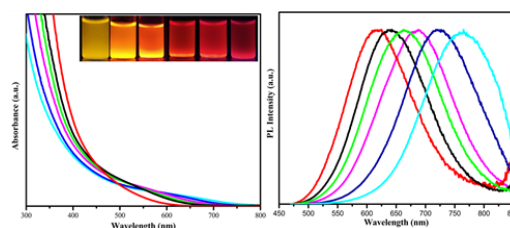


Keywords : Quantum dots, Aqueous synthesis, Surface functionalization, Optoelectronic properties, Photoanodes, Photovoltaics

General context, scientific issues :

Ever growing energy needs and the associated detrimental consequences pose significant challenges to the mankind. It becomes imperative to work towards developing alternative and eco-friendly sources of energy. Quantum dots (QDs), a class of semiconductor nanocrystals, are considered as one of the ideal zero-dimensional nanomaterials owing to their unique properties [1][2]. The bandgap of these nanomaterials can be easily tuned by varying their size, composition, or surface chemistry. Tunable bandgaps allow to absorb and emit light efficiently across a wide range of energies, enhancing the light absorption capabilities and enabling harvesting of a broader range of photons [3]. In addition, the bandgap tunability paves way for proficient energy transfer and recombination mechanisms leading to higher quantum yields and bright emission in photovoltaic applications. Thus, QDs are suitable candidates in energy harvesting devices such as solar cells [4].

Illustration : UV-vis and PL emission spectra of the synthesized Cu-In-Zn-Se/ZnS QDs while varying reactant molar ratios with inserted digit photograph taken under UV light illumination



Main results

A series of Cu-In-Zn-Se/ZnS QDs having high quantum yields have been prepared by employing a robust, quick, and inexpensive microwave-assisted aqueous phase-based synthesis approach. The synthesized QDs have been characterized via UV-visible and PL spectroscopy, DLS, XRD, TEM, photovoltaic and EIS techniques. The energy bandgap of Cu-In-Zn-Se/ZnS QDs was found to be tunable by control of their non-stoichiometry. Being in line with the variation of band gap, the synthesized series of QDs also exhibit a systematic PL tunability. Phase transfer of synthesized hydrophilic Cu-In-Zn-Se/ZnS QDs to organic phase was achieved by tuning their surface polarity. This allows the dispersion of Cu-In-Zn-Se/ZnS QDs in polar or in non-polar solvents as per desired application(s). It is anticipated that these results will pave the way for initial identification of best possible QDs to be integrated in full QDs-sensitized solar cells with the collaboration of international partners.

Objectives and stakes :

The objectives of the undertaken study are:

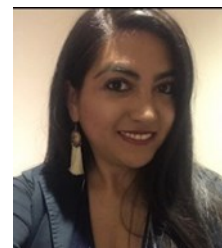
- Realization of environmentally benign, Cd-free Quantum dots (QDs) by developing a robust aqueous solution-based synthesis technique.
- Characterization of synthesized QDs to understand their optical, structural, and electrical properties.
- Preparation of TiO₂ photoanodes by PVD and deposition of synthesized QDs on prepared TiO₂ photoanodes by spin coating.
- Characterization of QDs sensitized TiO₂ photoanodes by photovoltaic and electrochemical impedance studies to understand their charge transport and recombination

Methodology :

The microwave-assisted aqueous phase-based synthesis of Cu-In-Zn-Se/ZnS QDs was performed by utilizing nitrate salts of In, Cu and Zn, suitable Se precursor, capping agent and surface ligand. The prepared solutions were microwaved in short pulses, resulting in the formation of Cu-In-Zn-Se and core/shell Cu-In-Zn-Se/ZnS QDs. The synthesis protocol was optimized by considering various factors, such as molar ratios of Cu/In/Zn/Se, selection of surface ligands (including GSH, TGA, 2-MPA, NAC, etc.), and pH conditions. These optimization steps were taken to ensure the desired properties and performance of the synthesized QDs. Possible non-stoichiometric effect in the QDs was also examined by altering the Cu/Zn reactant ratios. The prepared Cu-In-Zn-Se/ZnS QDs were characterized by performing UV-visible and photoluminescence (PL) spectroscopy, X-ray diffraction (XRD), and electrochemical impedance spectroscopy (EIS).

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Keywords : 3D printing, multi-material, plastic blend, recycling, , waste-based, Fused Granular Fabrication, distributed.

General context, scientific issues :

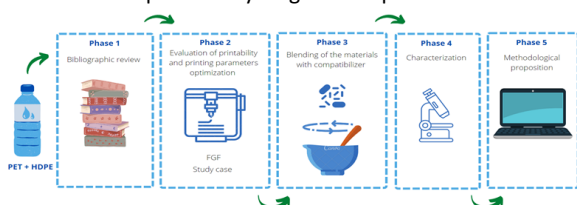
The societal awareness on plastic recycling have received an important attention by scientific, policymaker and general public. Unfortunately, the statistical analysis on the centralized recycling process proves that the valorization is far from being an efficient technique [1]. However, the strong development of 3D printing has allowed new ways of meeting society's various needs. In order to overcome this limitation, 3D printing (I3D) has made it possible to find new ways of responding via the distributed recycling of certain plastic wastes on a local scale [2,3]. Recently, the Fused Granular Fabrication (FGF) process has been introduced to 3D printing using polymer melts, reducing the number of melting/extrusion operations required to recycle the material. This technology opens the way to the use of new recycled materials [4], but one limitation is the impurities present in this waste, such as mixing with incompatible polymers, which reduce the properties of the materials. To address this issue, direct printing of multi-material post-consumer waste combined with the use of compatibilizers to improve the properties of polymer blends was explored in this study. Here, we considered a common waste product, a Cristalline© brand water

Objectives and stakes :

The major goal of the thesis is to solve the current issues presented in the local scale plastic recycling (polymer's mixture and compatibilization) via direct print technology. It includes 3 general goals. Firstly, study the feasibility of direct printing multi-material recycle plastic and its characterization. Secondly, evaluation of the blend behavior to the addition of compatibilizers which might allow the homogenization and enhancement of the material properties. Thirdly, the development of a methodology proposition of the distributed recycling approach on a local scale via 3D printing for multi-material plastics.

Methodology :

In order to develop the thesis objectives, five phases shall be considered as it appears in Fig 1. In the first phase, we evaluated different routes of compatibilization and determined the most suitable one in view of the direct blending via 3D printing and according to the literature review. Secondly, the development of several printing test using as feedstock the recycle water bottle Cristaline© (commonly used in France) to optimize the printing parameters and assess its printability. In the third step, PET and HDPE have been blended with a compatibilizer, followed by its mechanical, thermal, rheological and morphological characterization. Finally, a methodology will be proposed thanks to the results obtained with an economical local scale plastic recycling via FGF process.





Main results

At first, a systematic biographic analysis has been carried out regarding the compatibilization between PET and incompatible polymers to determine the most appropriate compatibilizer for our study. From the analysis concerning PET mixed with polypropylene or High density polyethylene (HDPE), the two most common compatibilizers used were reactive compatibilizers functionalized with maleic anhydride followed by non-reactive copolymers such as Poly (Styrene-co-Ethylene-co-Butylene-co-Styrene) copolymer (known as SEBS).

After collection, the bottle body and cap were separated to characterize each material chemically and thermally, and to determine the bottle's composition (~90% PET in the body and ~10% HDPE in the cap). Material characterizations have confirmed the structures and properties of the two initial polymers. In addition, the entire bottle, without separation of the two plastics, was processed for final printing by a series of operations that can be easily implemented locally: crushing, sieving, washing and drying. Next, the materials were mixed without compatibilizer in the FGF printer and the macroscopic properties of the objects were evaluated (e.g. tensile and Charpy tests). Finally, a functional object was printed. The results demonstrated the feasibility of using mixed post-consumer waste (PET/HDPE plastics) as a raw material for compatibilizer-free direct 3D printing, and the ability of the FGF 3D printer to produce objects on a large scale. Secondly, the use of three compatibilizers, both reactive and non-reactive, was tested to improve material properties and facilitate printing, and injected samples were pro-

References :

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<p>2023</p> 	<p>Research subject: Modeling of chemical and biochemical processes using advanced phenomenological and data-driven techniques</p> <p>Cindy Trinh (3rd year)</p> <p>Dimitrios Meimaroglou, Sandrine Hoppe</p> <p>Génie des Produits</p>	
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Keywords : artificial intelligence, machine learning, product engineering, quantitative structure-property relationship, molecular descriptors, thermodynamic properties, polymerization

General context, scientific issues :

Chemical Product Engineering (CPE) has numerous challenges such as the complexity of the products and of the link properties-structure-process, as well as the need to develop quickly new products with defined properties. Artificial intelligence (AI)/machine learning (ML) data-driven methods have shown very good performance in tackling complex problems in other areas and could therefore be very helpful to address CPE challenges, where classical approaches fail or are inefficient.

Objectives and stakes :

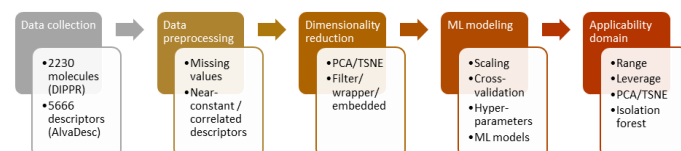
In this work, ML approaches are investigated for two applications in CPE. Each application has its own problem and data specificities, which will impact the adopted ML approaches.

- Application 1 consists in modeling of radical polymerization of styrene in presence of Ground Tire Rubber (GTR). Why ML? Knowledge-based modeling is very complex for this system (a lot of reactions and nonlinear phenomena occur simultaneously) and the grafting of polystyrene on GTR is not fully understood.
- Application 2 consists in predicting the thermochemical properties (enthalpy and entropy of formation) of a molecule from descriptors (i.e., structural and physicochemical features). Why ML? Quantum Chemistry or Group Contribution (GC) methods, commonly employed to calculate these properties, have shown limitations in terms of applicability to more complex/larger chemicals and/or computational costs.

Methodology :

- Application 1: First, an experimental procedure enabling a homogenous and controlled polymerization must be set up to produce enough data of good quality, necessary in any ML approach. Based on the obtained data, several ML techniques can be evaluated and combined with knowledge-based models.
- Application 2: The adopted methodology is typical of any ML project, but the major contribution of this work lies in the mapping of different methods at each step and in the evaluation of their impact on ML model performance (Figure 1). A wide diversity of molecules is also considered to obtain a larger applicability of the developed models for the discovery of reactive working fluids [1].

Illustration : Figure 1: Typical methodology for ML projects and the investigated methods in this work





Main results

- The state-of-the-art of ML in CPE resulted in a review article [2].
- Application 1: The developed experimental procedure and the results of ML modeling with the generated data are described in [3]. Gaussian Processes (GP) methods are being investigated due to their ability to provide predictions accompanied by uncertainties and due to their adaptability to incoming new data. The introduction of prior knowledge (based on available phenomenological models [4]) to GP improved the results, which were also physically more consistent.
- Application 2: The characteristics of the data (i.e., high dimensionality, large diversity of molecules) are particularly challenging and some methods seem less adapted (e.g., feature extraction, distance-based methods), especially due to the curse of dimensionality. Data preprocessing was performed to clean the data while limiting the loss of information. Feature selection methods enabled to identify the most relevant descriptors, thus improving interpretability, computation time while keeping similar performance as when all descriptors are considered. The identified descriptors remind the individual contributions of groups in GC approach. Applicability domain methods are being investigated to identify on which chemical structures the developed model can make reliable predictions. As descriptors display some limits, another powerful molecular representation (Graph Neural Networks) will be investigated in a future PhD thesis.

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 <p>2023</p>	<p>Research subject: Salts and pollutants management in supercritical water gasification processes</p> <p>Victor Vastra (3rd year)</p> <p>Hervé Muhr, Geert Haarlemmer</p> <p>Génie des Produits, CEA</p>	
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Keywords : Supercritical water, gasification, inorganic salts, pollutants, biofuels, black liquor, process engineering

General context, scientific issues :

Supercritical water gasification allows to produce gases from wet resources. Over 374 °C and 22.1 MPa, water becomes a highly reactive medium and promotes gasification reactions. This thesis focuses on black liquor which is a good candidate to study issues linked to inorganic content of wet resources.

Objectives and stakes :

The development of the process is at the laboratory pilot stage, with operating times limited to few hours. The main issues and research lines deal with corrosion problems and management of pollutants and inorganic species. When water reaches the supercritical state, it leads to the precipitation of salts contained in the resource [1] and thus to the clogging of the reactors [1-2]. This study will focus on solutions to understand the behaviour of these salts and their management.

Methodology :

First, a bibliographical study was carried out concerning the salts, their behaviour in supercritical water gasification and the solutions implemented in the literature. A second part of the study concerned the thermodynamic approach to predict the behaviour of inorganics (equilibrium diagrams of solid, liquid or gaseous phases as a function of temperature and pressure conditions). In parallel, the experimental work focuses on the characterization of black liquor and gasification products, with a special focus on inorganics. A second experimental part of the thesis concerns the study of organic salts that may precipitate in salt separator conditions. The ultimate goal is to increase the understanding of the behaviour of salts and pollutants in supercritical water conditions, and also in salt separator conditions, and to finally generate a numerical model based on experimental observations. With this knowledge, an evaluation of the different strategies for inorganics and pollutants management is expected, whether thermodynamically or chemically, and thus help the laboratory to propose design solutions for future supercritical water gasification pilots.

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Illustration : Precipitation of sodium carbonate in a continuous hydrothermal gasification reactor, leading to clogging of the device



Main results

Some salts precipitate directly under supercritical conditions (type-2 salts) while others can still be dissolved near critical point (type-1 salts). Literature shows that one way to remove salts out of reactors is to make the inorganic mix tend to a type-1 salt behaviour, playing on element ratio [3]. In this case, most of the salts can be solubilized by water and then removed as a salt-rich effluent after cooling at the bottom of devices, instead of being stuck on reactors' walls. Anyway, studies on black liquor under low and high temperatures, corresponding whether to separator or gasification conditions, show that the main precipitating salt is sodium carbonate, which is a type-2 salt.

In order to better understand why type-2 salts, such as sodium carbonate, are mainly prejudicial for the process, model mixtures of salts, according to the resource composition, have been studied with the use of additives in batch reactors to build a numerical model of global behaviour. As mainly suggested in literature, black liquor should be salt separated before it is introduced in the gasifier [4]. Nevertheless, separation at low temperature can generate new types of salts, such as organic salts, and it has not been mentioned in papers so far. Some model organic salts have been studied in this thesis, so as to understand their behaviour, predict their formation and classify them.



Keywords : Emulsions, Rheology, Pickering Emulsions, Soft Matter, Proteins, Interfaces

General context, scientific issues :

Protein-stabilized emulsions have attracted great attention in the last decades as they represent a good alternative to emulsions with surfactants that can be harmful to the environment. Proteins are one of the main agents for the preparation of emulsions in the food industry as they can be safely ingested, have an amphiphilic character, and provide favorable nutritional properties. Recently, plant-based proteins, such as Pea protein isolate, have gained a lot of interest because they allow the development of products that meet the major environmental challenges of today [1].

However, these are complex systems due to the nature of the proteins themselves. Indeed, they are highly dependent on formulation and processing conditions such as pH or emulsification protocol. One of the main characteristics that differentiate proteins from classical surfactants is their ability to change conformation depending on the surrounding properties and this translates into key modifications in the final emulsions. For instance, it is reported that proteins can behave as soft particles, stabilizers of what are known as Pickering emulsions, and in other cases they appear to have similarities to classical surfactants [2]. Due to this, predicting and controlling the properties of protein-stabilized emulsions remains a highly complex task of great industrial and fundamental interest.

Objectives and stakes :

Here we propose to study the interfacial properties of pea protein stabilized emulsions. Great attention is devoted to the stabilization mechanism and how this can affect the stability of the emulsions

Methodology :

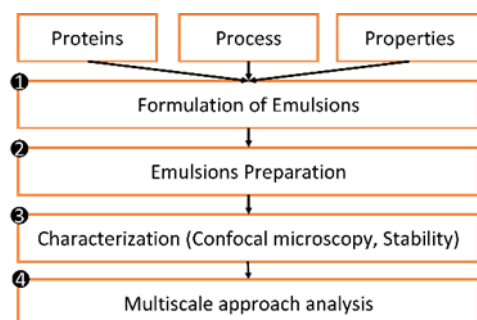
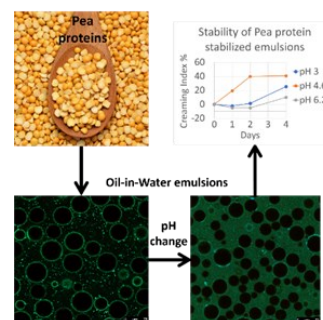


Illustration : Schematic representation of the protocol followed with protein-stabilized Pickering emulsions



Main results

Based on previous results obtained with animal-based proteins of Bovine Serum Albumin, a simple protocol to stabilize Silicone oil-in-water emulsions was implemented.

The emulsions were visualized with confocal microscopy by means of molecular rotors attached to the proteins. The stability of the emulsions was studied for several days. A characterization of the elasticity of the interfaces was performed by means of the molecular rotors, as well as an observation of how the stabilization mechanism varies as a function of a key property such as pH.

The results show a correlation between the elastic character of the interfaces and the stability of the emulsions, thus relating the mesoscopic scale to the macroscopic properties.

References :

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Keywords : Poly (lactic acid), liquid water diffusion, temperature, crystallinity, calculation method

General context, scientific issues :

Poly (lactic acid) (PLA) is a biobased and hydrolytically degradable aliphatic polyester that is gaining popularity as a sustainable alternative to petroleum-based polymers, aiming to mitigate their environmental impact [1]. In various fields, such as medical implants and packaging, a comprehensive assessment and fundamental understanding of water diffusion behavior in PLA are crucial. Water diffusion in PLA is a complex phenomenon influenced by several factors, for example, temperature and polymer crystallinity. Temperature plays a significant role in water diffusion behavior in PLA. Previous studies show that increasing temperature generally enhances the diffusion rate of water molecules within the polymer matrix. However, they are limited to the effect of temperature on water diffusion in PLA below or around 60 °C [2]. Further research is needed to explore the behavior of water diffusion at higher temperature which could be relevant for applications requiring higher temperature. Some studies suggest that a higher crystallinity leads to a lower water uptake due to a reduced amorphous phase available for water penetration [3]. In contrast, other research findings indicate that crystallinity may enhance water diffusion by creating preferential pathways for water molecules through the polymer matrix [4]. Therefore, the precise relationship between temperature, crystallinity, and the diffusion of liquid water within PLA remains inade-

Illustration : Water diffusion: an essential component in the life cycle of PLA



Main results

The water diffusion behavior in PLA at different temperatures and crystallinities is studied. M_m and D are estimated via Fick's second law. Figure (a) shows an increase of diffusivity on increasing the temperature, due to the augmented molecular mobility of both water and PLA at higher temperatures, thereby facilitating the diffusion process. Within the temperature range under investigation, the saturate water uptake (M_m) increases slightly with temperature and then levels off. Figure (b) shows the influence of crystallinity on water diffusion and saturate water uptake in PLA. When the crystallinity increases from 0% to 30%, the diffusion coefficient initially increases and then decreases. In contrast, the saturate water uptake exhibits an opposite trend. This suggests that a lower initial crystallinity results in a higher proportion of non-crystalline phase, facilitating water diffusion. However, as the crystallinity increases, the material becomes denser, impeding the diffusion of water molecules. The decrease in saturate water uptake can be attributed to an increase in the crystallinity, limiting water penetration. These findings are significant for understanding the water transport properties of the material and its relevant applications. Further research considering additional factors is needed to comprehensively evaluate the influence of crystallinity on liquid water diffusion in PLA.

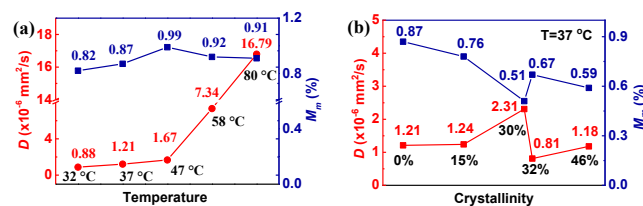
Objectives and stakes :

The objective of this study is to investigate the effect of temperature (32 °C, 37 °C, 47 °C, 58 °C, and 80 °C) and crystallinity (0%, 15%, 30%, 32%, and 46%) on liquid water diffusion in PLA. In particular, the temperature of 58 °C is selected due to its significance as a standard for PLA biodegradation tests and its proximity to the glass transition temperature (T_g) of PLA. To enhance the accuracy of estimating the water diffusion coefficient (D) and saturated moisture weight (M_m), a novel calculation method is proposed, aiming to surpass the limitations of traditional approximation methods.

Methodology :

- (1) Prepare PLA samples with varying crystallinity levels (from 0% to 46%).
- (2) Conduct temperature-controlled diffusion experiments by immersing samples at temperatures ranging from 32 °C to 80 °C.
- (3) Measure water diffusion using gravimetric method to assess uptake over time and establish diffusion profiles.
- (4) Analyze diffusion data using mathematical models to calculate diffusion coefficients (D) and assess the influence of temperature and crystallinity.

This experimental approach aims to investigate the effects of temperature and crystallinity on liquid water diffusion in PLA. The findings will contribute to our understanding of diffusion behavior and inform the development of PLA-based materials with optimized water diffusion properties.



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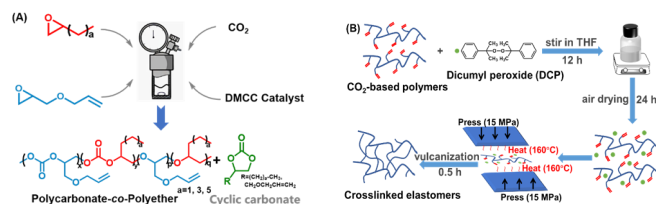


Keywords : CO₂ copolymerization, alkyl length, mechanical properties, terpolymer, elastomer

General context, scientific issues :

Using CO₂ as a raw material to synthesize new molecules and/or materials seems to be appealing to carbon sequestration process [1]. Various copolymerization processes of CO₂ with epoxides are described in the literature and CO₂-based plastics are industrialized [2]. There are no studies on the synthesis of CO₂-based elastomers and the effects of the alkyl length of epoxides and double bond content on the structures and properties of terpolymer.

Illustration : Preparation procedure of CO₂-epoxides (Figure A) and schematic diagram of cross-linked CO₂-based elastomer (Figure B).



Objectives and stakes :

This study aims to develop a process for synthesizing a CO₂-based elastomer, a terpolymer of carbon dioxide with long linear alkyl groups epoxides (i.e., 1,2-butene oxide (BO), 1,2-hexene oxide (HO), 1,2-octene oxide (OO)) and double-bond bearing epoxide (allyl glycidyl ether (AGE)). The emphases were on the effects of alkyl length of epoxides and double bond content on the polymer structure, glass transition temperatures (T_g) and mechanical properties.

Main results

Table 1. Molecular characteristics and mechanical properties of terpolymers

Entry	Feed	Conversion [%]	T_g [°C]	σ [MPa]	ϵ [%]
1	AGE/BO(5/95)	>99	5	2.2±0.3	654±68
2	AGE/BO(10/90)	>99	2	1.6±0.0	272±9
3	AGE/BO(20/80)	>99	-1	2.0±0.1	201±12
4	AGE/HO(5/95)	>99	-11	0.5±0.1	467±37
5	AGE/HO(10/90)	>99	-13	0.6±0.0	295±21
6	AGE/HO(20/80)	>99	-14	0.7±0.1	284±5
7	AGE/OO(5/95)	>99	-22	0.3±0.0	373±28
8	AGE/OO(10/90)	>99	-23	0.3±0.0	126±19
9	AGE/OO(20/80)	>99	-25	0.5±0.1	106±13

When the length of alkyl chains is the same, the T_g significantly decreases with increasing AGE content. This is because the AGE has a flexible pendant ether group. The T_g of terpolymer decreases with increasing alkyl length. This is because a long chain length increases the molecular chain flexibility.

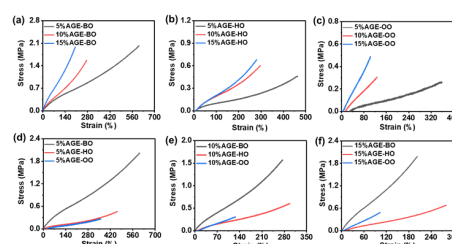


Figure (a)-(f) show tensile stress-strain curves of terpolymers with different alkyl lengths and double bond contents. When the length of alkyl chains is the same (i.e., figure (a), figure (b) or figure (c)), the elongation at break is negatively correlated with the crosslinking density, and the modulus of elastomer increases with the increase of the double bond content. With the same crosslinking density (i.e., figure (d), figure (e) or figure (f)), the shorter the length of alkyl chains, the higher the tensile strength and elongation at break.

Methodology :

(1) Coupling reaction of CO₂-epoxides

In a glove box, Zn-Co(III)DMCC catalyst and epoxides were charged into a pre-dried high-pressure reactor equipped with a magnetic stir. The autoclave was then taken out of the glove box and charged with 4MPa CO₂ at 60 °C. After a desired period of time, the autoclave was cooled with ice-water bath, then CO₂ pressure was slowly released. A small amount of crude product was removed for 1H NMR spectroscopy to determine the monomers conversion. The remained products were dissolved with dichloromethane and then precipitated by excess methanol to remove unreacted monomers and small molecule by-products. Then the precipitated polymers were collected and dried at 35 °C under vacuum for 48 h. A small amount of the purified product was removed for DSC measurements to determine the T_g .

(2) Preparation of cross-linked CO₂-based elastomers

First, 3.0 g CO₂-based polymers and 0.003 g dicumyl peroxide (DCP) were dissolved in 10 mL tetrahydrofuran (THF) and stirred for 12 h at room temperature. Then the residual solvent was further removed at room temperature for 24 h. The rest of the mixture was vulcanized at 160 °C under 15 MPa for 0.5 h. After the reaction was quenched, these specimens were left for 12 h before tensile testing. Three replicates for each sample were performed to determine the mechanical properties.

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- [1] Rapagnani R. et al., Nat. Chem. 2022, 14:877-883.
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SITE ENSIC

1, rue Grandville

BP 20451

54001 Nancy Cedex—France

Tél: +33 (0)3 72 74 38 00



SITE ENSAIA

2 Avenue de la forêt de Haye

TSA 40602

54518 Vandoeuvre –lès-Nancy– France

Tél: +33 (0)3 72 74 40 00



SITE IUT Nancy-Brabois

Bâtiment H2

Rue du Doyen Urion

54600 Villers Les Nancy

Tél: +33 (0)3 72 74 38 00



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