LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

PRESENTATION OF

PHD AND POST-DOCTORAL RESEARCH WORK

2023-2024

ABOUT

The LRGP is a joint research unit between the CNRS and the University of Lorraine, located in Nancy (Grand Est, 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 SIMPPÉ doctoral school. It has longstanding 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

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.

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 document, 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.

The direction team
hopes you enjoy reading.
Best regards,

Marie-Odile Simonnot
Director

Isabelle Chevalot
Deputy Director

Pierre-Alexandre Glaudes
Deputy Director

Sandrine Jadelot-Nalet
General Secretary

Research departments

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 gasliquid 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).

Research departments

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.

INDEX

PERSEVAL - Processes for Environnement, Safety and Resource Valorisation

INDEX

PRIMO - Processes, Reactors, Intensification, Membranes, Optimization

INDEX

BIOPROMO - Bioprocess, Biomolecules

INDEX

BIOPROMO - Bioprocess, Biomolecules

INDEX

CITHERE - Kinetics Thermodynamics Energy

INDEX

CITHERE - Kinetics Thermodynamics Energy

INDEX

PRODUCT ENGINEERING

INDEX

PRODUCT ENGINEERING

PERSEVAL

Processes for Environnement, Safety and Resource Valorisation

Implementation of electrodialysis in recycling processes for used cathode materials from lithium-ion batteries

By Soukayna Badre-Eddine, 1st year

Supervisors: Laurence Muhr, Alexandre Chagnes

Keywords

Electrodialysis | Lithium-ion batteries | Separation | Membrane processes | Hydrometallurgy

PERSEVAL

General context, scientific issue

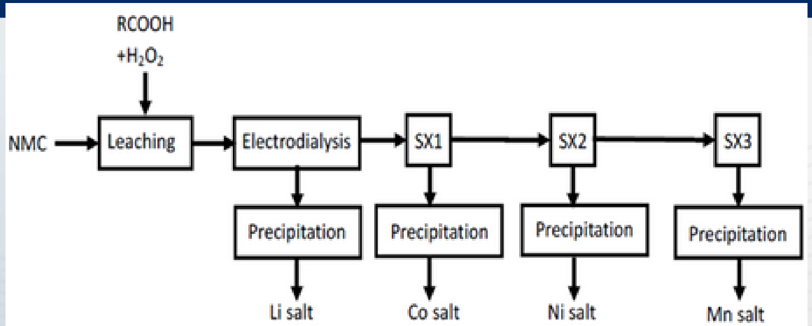
Electrodialysis is emerging as a technique with interesting potential for use in hydrometallurgy processes for recycling Li-ion batteries. [1]. A limitation may, however, be linked to membrane clogging due to the precipitation of metals in the membranes from the battery's black mass leaching solutions. This leads to a loss of performance of the electrodialyzer and premature aging of the membrane [2].

Methodology / Experimental approach

Organic acid will be employed for their ability to dissolve NMC electrodes and form anionic complexes within the optimal pH range for electrodialysis. In this work, we propose to study the impact of leaching conditions with citric acid as a leaching agent for the metal cations Ni2+, Co2+, and Mn2+ on the speciation of the present compounds. This process allows to separate lithium from other multi-charged cations, in the form of anion complexes, present in the leach solutions of NMC cathode materials to pass through anion exchange membranes, while lithium, which does not form a complex, is transported across cation-selective membranes. This characteristic is crucial for ensuring the selectivity of lithium recovery and reducing the risk of membrane fouling during electrodialysis operations.

The electrodialysis operation will be accompanied by:

- The study of a protocol for monitoring the limit current during the process
- Monitoring of membrane aging (alteration, clogging)
- Optimization of the electrodialysis step (selectivity and faradic yield)



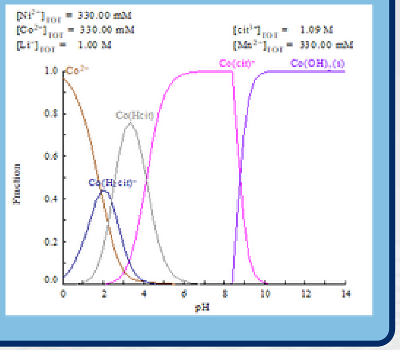
The overall scheme of the proposed hydrometallurgical process to produce high quality salts of cobalt, nickel, manganese and lithium.

Objectives and stakes

This project aims to adapt the chemistry of the overall hydrometallurgical process to avoid chemical clogging of the membranes while maintaining the selectivity of the process. For that, the metal precipitation into the membranes can be delayed by using conventional electrodialysis combined with complexation. Therefore, an overall flowsheet including leaching operation with carboxylic acid, liquid-liquid extraction/precipitation and electrodialysis in carboxylic medium will be developed in order to produce high-grade salts of cobalt, nickel, manganese and lithium.

Main results

- The study of speciation using the Medusa software showed that Ni2+ Co2+, and Mn2+ form anionic complexes with citric acid at pH 5, unlike Li+, which does not form a complex with the citrate- anion.
- A study on the leaching of NMC111 with citric acid in the presence of H2O2 as a reducing agent was conducted to identify the optimal pH for the formation of anionic complexes (metal citrate) while maintaining a high leaching yield.



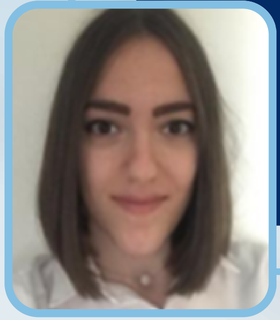
To determine the optimal leaching conditions, various experiments were carried out by varying parameters such as the solid-liquid ratio, reaction time, leaching temperature, and the volumetric percentage of H2O2.

- Leaching conditions that result in a treatable solution with a pH of 5 were achieved
- Solutions with the same composition as the leaching solution will be treated by electrodialysis.
- The selectivity of lithium recovery after transfer through the cationic membrane will be studied.

References

[1] S. Gmar et A. Chagnes, « Recent advances on electrodialysis for the recovery of lithium from primary and secondary resources », Hydrometallurgy, vol. 189, p. 105124, nov. 2019, doi: 10.1016/j.hydromet.2019.105124.

[2] S. Gmar, A. Chagnes, F. Lutin, et L. Muhr, « Application of Electrodialysis for the Selective Lithium Extraction Towards Cobalt, Nickel and Manganese from Leach Solutions Containing High Divalent Cations/Li Ratio », Recycling, vol. 7, no 2, p. 14, mars 2022, doi: 10.3390/recycling7020014.



Selective recovery of precious metals from waste electrical and electronic equipment (WEEE) by electrochemical methods using ionic solvents

By Calogera Bertoloni, 3rd year

Supervisors: Éric Meux, François Lapicque,
Sophie Legeai

Keywords

Precious metals | Deep eutectic solvents | Electroleaching | Electrodeposition | WEE

PERSEVAL, CEM (IJL)

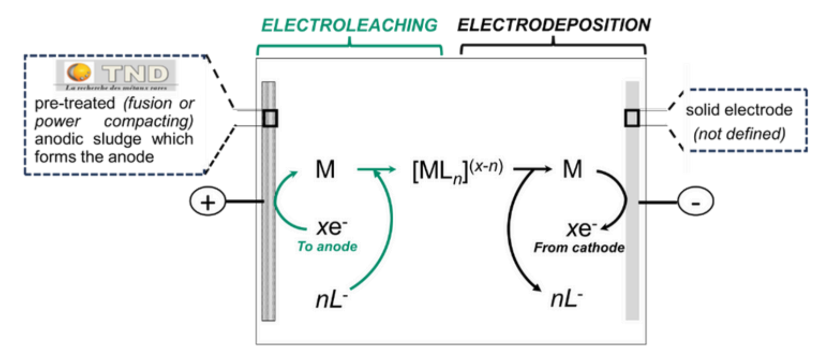
General context, scientific issue

One day without a cell phone, is it possible in 2024? These metal-rich objects have become indispensable. Indeed, their metal contents particularly for precious metals (Au, Ag, Pd), is far higher than that of primary resources. Their recycling thus appears essential.

Methodology / Experimental approach

The mixture of choline chloride (ChCl) (hydrogen bond acceptor) and ethylene glycol (EG) (hydrogen bond donor) called ethaline (ET), was selected as a DES following the first studies.1 To make this process even more environmentally friendly, the substitution of ET with a natural deep eutectic solvent called propeline (PROP) is considered. EG is thus replaced by propylene glycol (PG) which is far less toxic and often used in cosmetic and pharmaceutical products.

Then, PROP and ET were compared when used in the electrochemical cell, indicating comparable performance in the leaching of Au, Ag and Pd.



Cell of the electrochemical process for the treatment of anodic sludge. M is for metal and L for ligand provided by DES (Cl-).

Objectives and stakes

Hence, the EE4Precious project, funded by ANR, focuses on the development of an electrochemical process which aims to couple two steps: electro-leaching and electrodeposition. The use of "Deep eutectic solvents" (DES), complexing, conductive, low-viscosity and liquid solvents, is favourable to ensure optimum efficiency of both steps.

Main results

Increasing temperature gives PROP with molar ratio (ChCl:PG) (1:3) similar phyco-chemical properties to ET1:2 in terms of viscosity and conductivity. Indeed, changing the molar ratio allows to reduce PROP melting temperature whereas increasing the temperature reduces its viscosity and increases its conductivity. The PG is a good alternative to EG for the electrochemical process. The electrochemical oxidation of the three precious metals is efficient and can be selective in PROP1:3.2

Due to the strong complexing activity of these solvents, the electroleaching step is efficient (yields close to 100%). The cyclic voltammetry of three separated metals shown that the reduction of the three complex ions is possible for their selective electrodeposition without degradation of the solvent.

The first results on polymetallic solutions are promising. In fact, the deposition tests carried out on solutions containing 50:50 (Ag:Au) molar ratio show that gold can be recovered first. This aspect will be studied with the continuation of the work, as part of Cyclamet PEPR, Recycling, strategic metals axis.

References

[1] Villemejeanne, B., et al , E. J. Environ. Chem. Eng. 2022, 10 (3), 108004.
[2] Bertoloni, C.; et al. Environ. Sci. Adv. 2024, 3 (6), 875–884.

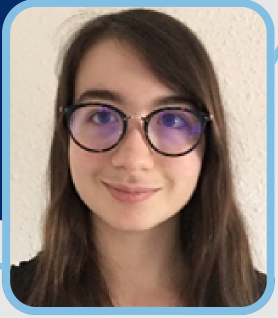
Influence of the geometric structure of filtration media on their performance

By Elise Cabaset, 2nd year

Supervisors: Dominique Thomas, Nathalie Bardin-Monnier, Augustin Charvet

Keywords

Permeability | Filtration | Fibrous media | Aerosol | CFD | Experiment



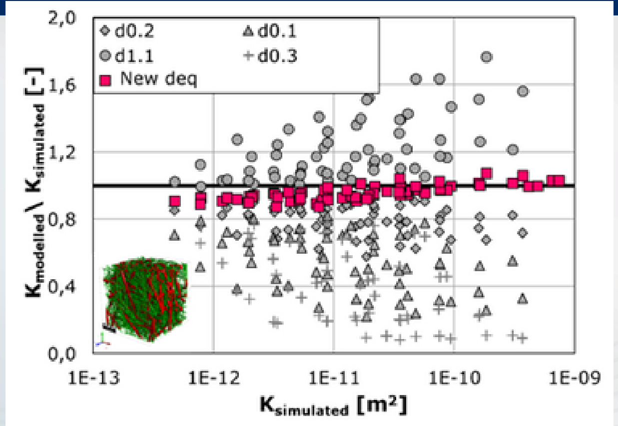
PERSEVAL

General context, scientific issue

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. Their performance can be assessed not only in terms of efficiency but also in terms of pressure drop, which depends particularly on their permeability.

Methodology / Experimental approach

One alternative to overcome these experimental biases is the use of numerical tools, such as Geodict (2022), to build perfectly characterized 3D structures and describe them in terms of permeability. Initially, 66 bimodal structures were created with different combinations of diameters and packing density ranging from 1 to 20%. More complex structures were then generated in Geodict, with trimodal, quadrimodal and decamodal fiber distributions. Finally, to extend the approach to more realistic fibrous media, numerical structures following lognormal and normal fiber size distributions were also created. In these cases, the diameter of each individual fiber constitutive of the non-woven media could be extracted, resulting in structures composed of 477 to 1995 fibers.



Comparison of simulated and modelled permeabilities of bimodal structures using equivalent diameters (deq) from the literature and the newly developed expression

Objectives and stakes

A nonwoven filter medium is a complex structure consisting of random arrays of fibers that present a varying size distribution. To determine filter permeability theoretically, these complex fiber structures are assimilated to structures composed of a single equivalent fiber diameter. Various models have been proposed in the literature to determine the permeability of complex fibrous media [1-3], and no consensus has been reached. Moreover, the experimental determination of permeability is difficult due to numerous uncertainties, including the measurement of media thickness and the structure of the media, particularly its fiber size distribution.

Main results

A new correlation has been developed, inspired by the previous work of the team [4], which yields smaller discrepancies between simulated and modelled values in a wider range of packing densities and diameters compared to those of the literature. These conclusions have also been validated with experimental and numerical data from the literature.

Some consideration has been conducted on using this theoretical approach as a decision-making tool. Since permeability is directly related to design, different media can have varying packing densities and equivalent diameters while maintaining the same permeability. It is also important to note that for each equivalent diameter, an infinite number of distributions are possible.

Media with known fiber diameters, composition and grammage are manufactured by Alkegen using an experimental protocol inspired by a papermaking process. Experimental tests on permeability and particle filtration efficiency using KCl and DEHS are currently underway on these various media. The main objective is to validate the new theoretical approach regarding permeability, and then to continue the study on aerosol filtration. Correlations of single-fiber efficiency by diffusion, interception or inertia will be extended to the case of bimodal or even multimodal fiber size distributions.

References

[1] Tafreshi H. et al., Chem. Eng. S. 2009;1154–1159
[2] Brown R.C. et al., Powder Technology 2001;3–9.
[3] Mattern K.J. et al., AIChE J. 2008;32–41.
[4] Thomas D. et al., Can J Chem. Eng. 2022;1-13

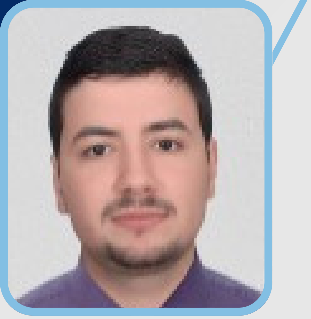
CO_2 conversion, wastewater treatment, electrochemical advanced oxidation process

By Saad Diris, 1st year

Supervisors: Emmanuel Mousset, Marie-Noëlle Pons

Keywords

CO_2 conversion | Wastewater Treatment | Electrochemical advanced oxidation process



PERSEVAL

General context, scientific issue

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 CO_2 in the atmosphere from treatment plants can be an environmental concern.

Methodology / Experimental approach

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 ($NaHCO_3$). Since the solution pH is varying during the electrochemical treatment, the influence of pH on the carbonates conversion into CO_2 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.

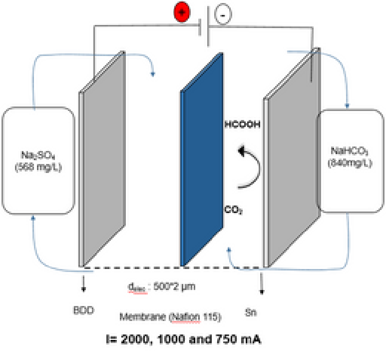


Figure 1: Experimental setup.

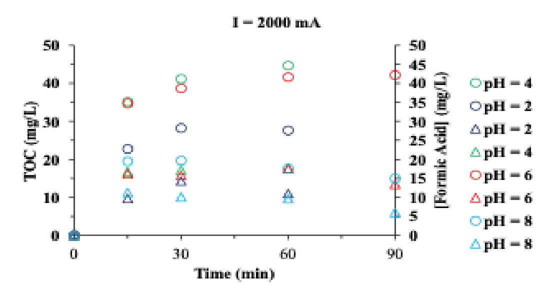


Figure 2: Evolutions of formic acid concentration ◯) and of TOC (Δ) as a function of electrolysis time and solution pH.

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 CO_2 generated during the mineralization of organic pollutants in wastewater by converting it into added-value organic compounds such as formic acid. In addition, the CO_2 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.

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 CO_2 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.

Multiphase flows at different scales: drop coalescence at liquid-liquid interfaces

By Yingjie Fei, 1st year

Supervisors: Huai-Zhi Li, Youguang Ma

Keywords

Multiphase flows · Interfacial phenomena · Various scales · Coalescence · Scaling laws · Flow fields

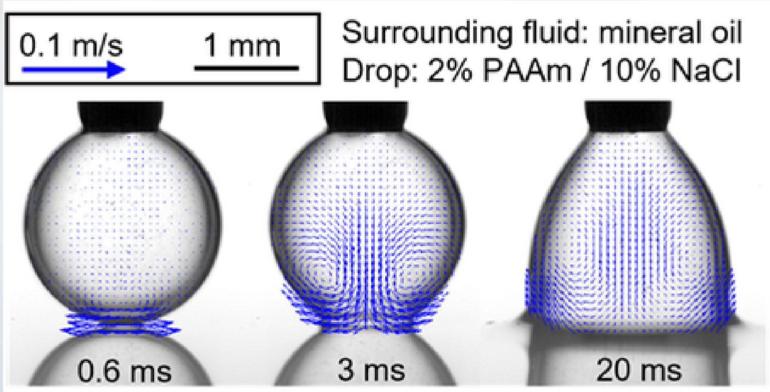
PERSEVAL, SYSPOL

General context, scientific issue

Multiphase flows with complex and ultra-fast interfacial phenomena are still poorly understood. This is the case of drop coalescence at a liquid-liquid interface, with a serious lack of investigations under very short time scale below ms and small space scale around μm [1-3].

Methodology / Experimental approach

Three cutting-edge techniques: a home-made ultra-high-speed direct current (DC) electric device with an acquisition frequency up to 1.25 MHz, a home-developed high-speed micro-particle image velocimetry (micro-PIV) up to 5000 flow fields/s and a high-speed camera up to 100000 frames/s, are employed in this work to monitor the coalescence size, drop shape evolution and resulting velocity fields inside the drop during the fast coalescence.



The velocity field inside a coalescing drop

Objectives and stakes

Drop coalescence is of both academic and industrial interests. Its complex dynamical behavior has fascinated researchers in different disciplines for a long time. Investigation on this topic under different scales, using both active and passive approaches, is contributing to a better understanding of physical mechanisms involved. These knowledges are essential for various industrial processes such as emulsification, coating, oil recovery, inkjet printing, etc.

Main results

Drops of four fluids with different rheological properties coalesce with the underlying phase in air and two surrounding oil phases, respectively. When drops coalesce at an air-liquid free surface, time evolution of dimensionless liquid bridge width is found to follow a scaling law: inertial limited viscous (ILV) regime $\Phi\sim\tau$ and inertial regime $\Phi\sim\tau1/2$, which is consistent with results reported in literature. When the coalescence occurs at a liquid-liquid interface, the viscous effect of the surrounding oil significantly retards the expansion of the liquid bridge, and the exponent of the ILV regime thus deviates from 1 to about 0.9. Notably, the transition between the two regimes is longer, which favors the analysis of control parameters. The flow fields measured by micro-PIV shows that the viscous force of the surrounding liquid induces significant vortices inside drops, which is different from what is observed in air. In addition, the flow fields in non-Newtonian drops are not only present near the liquid bridge, but also distributed throughout the drops due to elasticity.

References

[1] Houssainy S. et al., Phys. Fluids. 2020, 32(5):052101.
[2] Zhang Q. et al., Phys. Rev. E. 2019, 100(3):033112.
[3] Li H. et al., Colloid. Surface A. 2024, 683:133066.

Study of the influence of activated sludge reactor hydrodynamics on antibiotic resistance development

Miguel Ángel Flórez Prieto, 1st year

Supervisors: Olivier Potier, Christophe Merlin

Keywords

Reactors
Wastewater Treatment
Activated sludge
Hydrodynamics
Antibiotic resistance
RTD
Tracing
Modelling

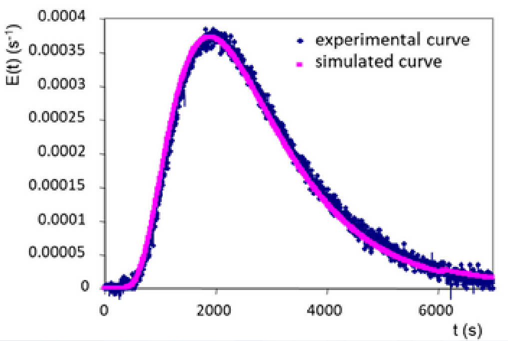
PERSEVAL

General context, scientific issue

Wastewater treatment plants occupy a key position in such way that it progressively became the final control point before releasing contaminants of emerging concern in the downstream environment. However, several contaminants became widely considered as emerging concern as more pernicious in the long term. These include pharmaceuticals but also biological pollutions such as antibiotic resistances.

Methodology / Experimental approach

The project is subdivided in complementary parts. The first part consists in designing, implementing, and comparing the performances of several wastewater lab-scale reactors differing by their hydrodynamic regimes. The idea is to promote defined hydrodynamic regimes favoring the activity of specific microorganisms leading the performance of the reactors. The performances of the reactors will be assessed using conventional parameter as well as the degradation of a selection of pharmaceuticals and using high standard molecular biology approaches: metatranscriptomics, HT-qPCR and qPCR (antibiotic resistance gene profiling and quantification), RTqPCR (expression of functions relevant to resistance dissemination). But firstly, hydrodynamics of the different reactors must be characterized and modelled with different approaches: tracing experiments, fluid mechanics, flow visualization, etc. RTD (Residence Time Distribution) experiments are used to check that pilot plants are well designed, and they can express hydrodynamic behavior notably between the CSTR and the plug flow reactor with axial dispersion with high Peclet number (low dispersion). Moreover, the Sensitivity of the hydrodynamic behavior to liquid flow rate changes must be also checked.



Example of RTD of a such reactor pilot plant

Objectives

- Use innovative design approaches to develop new treatment processes based on the control of the hydrodynamics of reactors.
- Improve their performances regarding the degradation of micropollutants, by changing reactor hydrodynamics.
- Control of antibiotic resistance release.

Expected results

The first phase of the project is based mainly on an analysis of the available literature on the topic of active sludge treatment and also on genes that generate bacterial resistance. Simultaneously with this, hypotheses are generated about the effect of hydrodynamics on water treatment that will be contrasted with the experimentation carried out in the coming years: the first is that a reactor configuration with a high Peclet (Pe) number can function as a barrier in matters of management of micropollutants, the second confers that hydrodynamics can generate greater biological diversity can lead to a decrease in the expression of genes that can lead to Bacterial resistance,

References

[1] G. PITRUZZELLO et al. Multiparameter antibiotic resistance detection based on hydrodynamic trapping of individual E. coli. Lab on a Chip, (2019). 19(8), 1417–1426. https://doi.org/10.1039/C8LC01397G.

[2] N. JOURDAN, T. NEVEUX, O. POTIER, M. KANNICHE, J. WICKS, I. NOPENS, Y. LE MOULLEC "Compartmental Modelling in chemical engineering: A critical review" (2019) Chemical Engineering Science, 210, 115196.

[3] R. HATOUM, O. POTIER, T. ROQUES-CARMES, C. LEMAITRE, T. HAMIEH, J. TOUFAILY, H. HORN, E. BOROWSKA "Elimination of Micropollutants in Activated Sludge Reactors with a Special Focus on the Effect of Biomass Concentration" (2019) Water 11 (11), 2217-2235.

[4] R. HREIZ, O. POTIER, J. WICKS, J.M. COMMENGE, "CFD Investigation of the effects of bubble aerator layouts on hydrodynamics of an activated sludge channel reactor (2019) Environmental technology, 40 (20), 2657-2670.

Experimental study of the chemical effects on the clogging of a solution filter in aprp and ag conditions

By Mtoilibou Abdallah Keymoon, 2nd year

Supervisors: Marie-Odile Simonnot, Laurent Cantrel

Keywords

LOCA (Loss Of Coolant Accident) | Clogging | SA (Severe Accident) | Filter | Chemical effects

LRGP, IRSN

General context, scientific issue

A 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-AES, MEB-EDX, DRX and IFTR-ATR.

Methodology / Experimental approach

The first part is devoted to small-scale experiments (~1L) aiming at studying the dissolution of debris and the potential formation of precipitates under conditions representative of a LOCA or SA (Figure 1). The solution contained H3BO3 and NaOH at two different concentrations. The tests were performed under two conditions: C2 campaign conditions (140 mM H3BO3 and 15 mM NaOH) at a pH of 7.5, and C3 campaign conditions (309 mM H3BO3, 64 mM NaOH, and 10 mM Borax) at a pH of 7.77. These experiments were carried out at temperatures of 40, 60, and 80 °C. The amounts of silicon, calcium, and zinc released by the debris were measured using ICP-AES. To evaluate the reactivity of these elements, tests were carried out with model solutions at 60 °C for periods ranging from 24 to 48 hours. Other elements such as iron and cesium (in the case of SA) were included in the study. The precipitates obtained were filtered through a Büchner filter. After drying in an oven at 60 °C, the precipitates were characterized using various techniques: IRTF-ATR, MEB-EDX, DRX, DRS, and Tof-SIMS. At the same time, the tests were simulated using the CHESS software in order to identify the precipitates and to assess the agreement between the experimental results and the simulations.

Finally, tests are carried out under conditions in the recirculation loop to determine the extent of the chemical effects on the pressure drop of the filters (Figure 2).

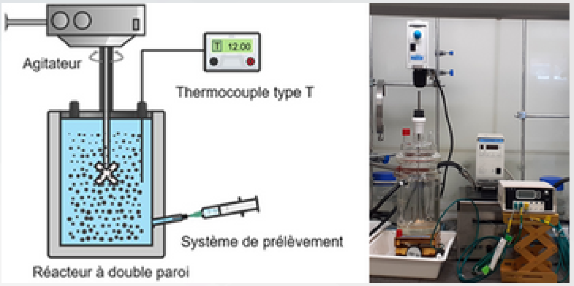


Figure 1: Scheme and photograph of the experimental set-up for static tests (COPINES)

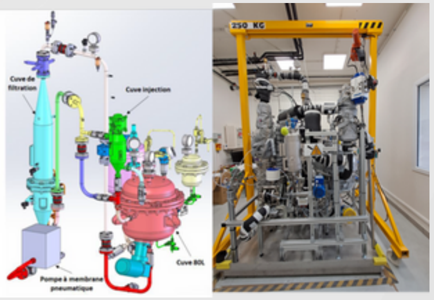


Figure 2: Scheme and photographs of the COPIN filter loop [3]

Main results

Dissolution tests were carried out on debris likely to be generated in the event of LOCA for nuclear reactors were carried out. The aim was to determine the dissolution kinetics of the main debris elements. The tests were carried out in a matrix of boric acid and sodium hydroxide solution, according to the conditions of the reactor type, at different temperatures and pH values. The dissolution of debris such as insulation fibers, concrete and the corrosion of metal surfaces was carried out. It appeared that the Si came mainly from the fibers, Ca from the concrete, and Zn from the corrosion of metal surfaces. These results will allow tests to be carried out with model solutions containing Si, Ca, Zn and Fe to investigate the chemical effects that may occur. Initial results show that the presence of Zn and Fe promotes reactivity. In addition, the presence of amorphous precipitates such as silica, calcium borates, borosilicates, zinc silicate and iron silicates were obtained at 60°C over a period of 24 hours. A comparison between the experimental data and those calculated using the CHESS software showed good overall agreement in terms of trends.

References

[1] D. JACQUEMAIN, « Les accidents de fusion du cœur des réacteurs nucléaires de puissance-État des connaissances?, sous-chapitre 7.1, IRSN », EDP Sci. Collect. Sci. Tech., 2013.

[2] « Livre de connaissances - Enjeux méthodes et applications des EPS niveau 2 - E. RAIMOND ».

[3] C. Le Maout-Alvarez, « Étude expérimentale des effets chimiques sur le colmatage des filtres dans l'industrie nucléaire », These de doctorat, Université de Lorraine, 2023. Consulté le: 12 décembre 2023. [En ligne]. Disponible sur: https://www.theses.fr/2023LORR0015

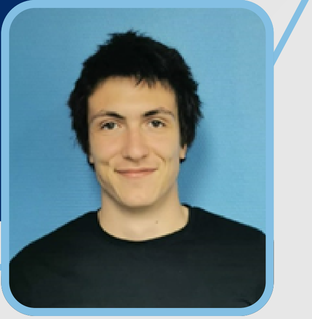
Metal recovery by agromining in French Guiana

By Thomas Monot, 3rd year

Supervisors: Baptiste Laubie, Marie-Odile Simonnot

Keywords

Agromining
Aluminum
ICP-OES
Hydrometallurgy
French Guiana



PERSEVAL, SOLEO

General context, scientific issue

Agromining is the process of extracting metals with hyperaccumulator plants. Initially developed to extract nickel, its potential is now being investigated for other elements like aluminium, as field campaigns have led to the discovery of numerous aluminium hyperaccumulators in French Guiana.

Objectives and stakes

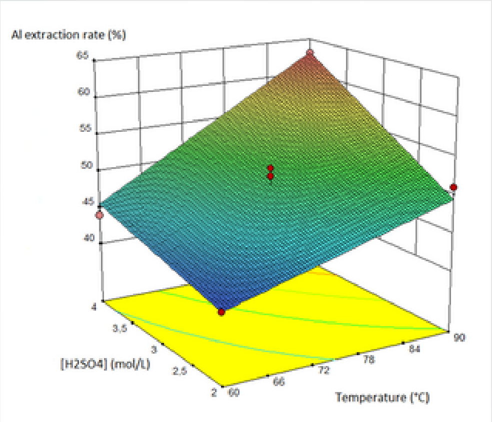
The first objective of the work presented here is the characterization of the biomass and ash of an aluminum hyperaccumulator from French Guiana, Qualea rosea. Following this characterization step, an aluminum recovery process using the ash of Qualea rosea will be developed by first screening the main factors impacting its extraction using the design of experiments methodology. Then, the extraction process will be further modified to eliminate the calcium, a major impurity in the ash.

Methodology / Experimental approach

Thermogravimetric analysis of Qualea rosea biomass was carried out to identify an appropriate incineration temperature for ash production. Both the ash and biomass elemental composition were analyzed by an organic analyzer and ICP-OES. X-ray powder diffraction analysis were also performed on the ash to characterize its crystalline phases.

Aluminum leaching experiments were carried out in borosilicated glass round flasks fitted with a thermometer, a water condenser and a magnetic stirrer on a heating plate using sulfuric acid as the leaching solvent. Aluminum and other elements extraction rates were determined by ICP-OES analysis of the leaching solutions. Scanning electron microscopy analysis were performed on the residue, as well as X-ray powder diffraction analysis when possible.

Two design of experiments were used in this work. The first was a simple factorial design aiming at studying the impact of temperature, sulfuric acid concentration and leaching duration on the aluminum extraction rate. The second was a Box Behnken design studying temperature and sulfuric acid concentration in leaching experiments with a higher solid/liquid (s/l) ratio.



Graphical representation of the aluminum extraction rate as a function of the temperature and sulfuric acid concentration at a solid/liquid ratio of 5%.

Main results

Characterization of the biomass confirmed Qualea rosea is an aluminum hyperaccumulator, its concentration in biomass being above the threshold for tropical plants at 4% in mass (1). Ash were produced at a 900°C temperature, and their elemental analysis showed they contained more than 25% aluminum in mass, and around 15% calcium.

Preliminary screening of the impact of three factors showed temperature was the main driver of aluminum extraction, 100% extraction being reached at low sulfuric concentration or for short leaching duration at a s/l ratio of 0.5%. Leaching experiments were then carried out at a higher solid/liquid ratio of 5% and at higher sulfuric acid concentrations to trigger calcium precipitation as calcium sulfate. Aluminum extraction in these conditions is lower, and the impact of temperature and sulfuric acid concentration have similar impact (Figure 1). The poorer performance of the leaching at 5% s/l ratio are attributed to the formation of a calcium sulfate passivation layer on the ash inhibiting the aluminum dissolution, a phenomenon described in the literature (2)

References

1. Metali F, Salim KA, Burslem DFRP. Evidence of foliar aluminium accumulation in local, regional and global datasets of wild plants. New Phytologist. 2012;193(3):637-49.
2. Seidel A, Sluszny A, Shelef G, Zimmels Y. Self inhibition of aluminum leaching from coal fly ash by sulfuric acid. Chemical Engineering Journal. 8 mars 1999;72(3):195-207.

Development of a low-tech process for the production of nickel from hyperaccumulator plants in a tropical context

By Clémence Pinchaux, 1st year

Supervisors: Marie-Odile Simonnot, Baptiste Laubie

Keywords

Agromining Nickel Hydrometallurgy Low-tech

PERSEVAL, ECONICK

General context, scientific issue

Nickel hyperaccumulators have been identified in a tropical region and can be cultivated on nickel-rich soils, allowing the development of nickel agromining in this region. The aim of this thesis is to develop a low-tech process for nickel production from these plants.

Objectives and stakes

The first aim of this project is to optimize the leaching of the biomass in order to maximize the extraction yield of nickel and the concentration of nickel in the leachate. To achieve this, various factors will be investigated, such as the preparation of the biomass by grinding or using biological processes, and the conditions of leaching, such as temperature, duration or pH. The second step is to isolate the nickel from the leachate.

Methodology / Experimental approach

The plants are ground and sieved to control the granulometry, then oven dried until the mass stabilizes before being leached. Several factors are investigated and the Design of Experiment (DOE) method is used to determine their influence. Plants are leached in an aqueous solution for a period of time and the mixture is then filtered. The plants and leachates are analyzed by ICP-OES, in particular to determine their nickel concentration. The extraction yield is calculated as the ratio of the mass of nickel in the leachate to the mass of nickel in the plants. The second stage of research will focus on the recovery of nickel from the leachate. Selective precipitation in hydroxide or carbonate form is not possible directly on the leachate as nickel is highly complexed with organic ligands. It is therefore necessary either to use a strong complexing agent or to chemically or biologically degrade the organic matter prior to precipitation.

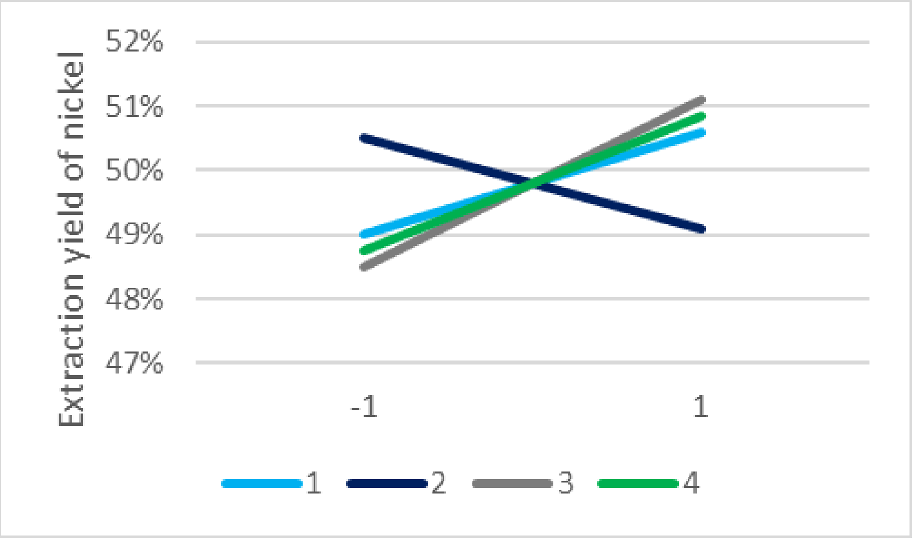


Diagram of effects from a DOE for four different factors

Main results

The first experimental design showed that the factors had little effect on the nickel extraction yield in the area studied. The average yield obtained was 50% with a standard deviation of 7%. Of the four factors studied, factors 3 and 4 had the greatest effect on leach yield and their effect was positive. These trials have enabled these four factors to be established and further trials are underway to investigate the effect of other factors and maximise extraction yield.

References

[1] Barbaroux, R., Meunier, N., Mercier, G., Taillard, V., Morel, J. L., Simonnot, M. O., & Blais, J. F. (2009). Chemical leaching of nickel from the seeds of the metal hyperaccumulator plant Alyssum murale. Hydrometallurgy, 100(1-2), 10-14.

[2] Guilpain M., Laubie B., Zhang X., Morel J.L., Simonnot M.O. (2018). Speciation of nickel extracted from hyperaccumulator plants by water leaching. Hydrometallurgy, 180, 192-200.

Membrane processes to minimize the environmental impacts of nickel valorization by agromining

By Thomas Porqueddu, 3rd year

Supervisors: Baptiste Laubie, Marie-Odile Simonnot

Keywords

Nanofiltration
Hydrometallurgy
Simulation
SEDE
Speciation
Recycling
Agromining

PERSEVAL

General context, scientific issue

This work falls within the context of the agromining chain, which aims to recover metals extracted from soils using plants. [1] 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 first 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. Then, a process study is made in order to determine the quantity of acid which can be recycled. Finally, a technico-economic analysis is proposed in order to assure the viability of these recycling method.

Methodology / Experimental approach

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 WATEQ4 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) [2] model coupled with PHREEQC simulation. 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. This knowledge is then used to estimate how much acid is able to be recycle using Matlab and VBA simulation.

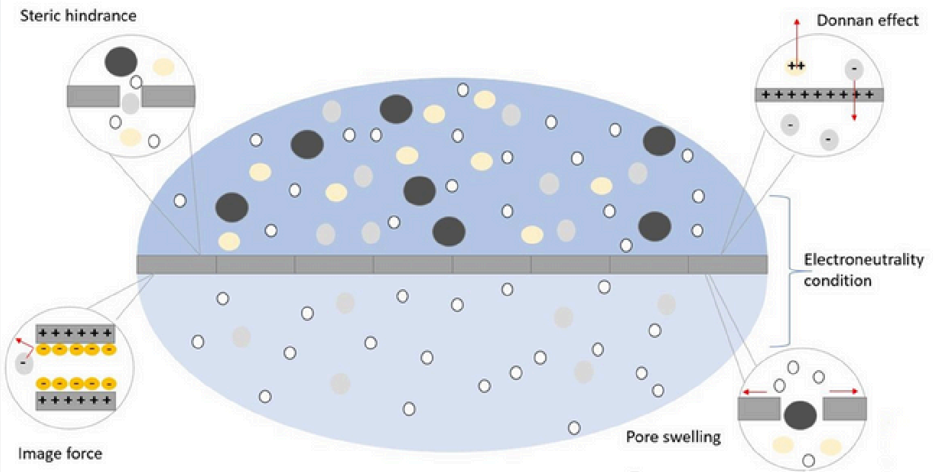


Diagram of the transport phenomenon considered model

Main results

The results of nanofiltration and transport modelling of a hyperaccumulator leachate highlight the interest of taking speciation into account. By considering the formation of ion pairs in the solution, it is possible to significantly increase simulation accuracy. The most striking example concerns nickel, magnesium and iron, where the difference between experimental and simulated values has been reduced from 10 to 2%, from 11 to 3% and from 10 to 2% respectively.

The simulation shows, even at the filtration optimum, that the separation is never perfect. Therefore, by using recycled acid, the ionic force rises and cause a decreased rejection rate.

This result shows the limit of the process. The study estimates that a maximum of 81% of acid is able to be recycled by using nanofiltration technology.

References

[1] Houzelot, V. et al. Chemical Engineering Research and Design 2017, 129, 1-11
[2] Lanteri, Y. et al. Journal of Colloid and Interface Science 2009, 331, 148-155

Impact of airborne nanoparticles on workers' health: a new method based on Krypton gas adsorption

By Olivier Rastoix, 2nd year

Supervisors: Sihane Merouane, Cécile Vallieres, Davy Rousset

Keywords

Safety | Surface characterization | Nanoparticles | Gas adsorption

INRS, PERSEVAL

General context, scientific issue

Engineered nanomaterials in powder form are increasingly used in industry for these last two decades, leading to legitimate concerns about their impact on health. Furthermore, several studies have shown evidence of surface area being a relevant criteria to estimate potential toxicological effects of nanoparticles [1-2]. Therefore, measuring the surface area of airborne nanoparticles could be a useful tool for occupational exposure assessment related to biological effects but remains a complex analytical challenge.

Objectives and stakes

This study aims to develop two methods for determining the specific surface area of a small quantity of nanomaterial collected from occupational airborne. The first method consists in adapting the specific surface area measurement by gas adsorption to a small quantity of material collected on an appropriate filter media. The second one aims to determine this surface area by a fully automated morphological analysis of images obtained by electron microscopy.

Methodology / Experimental approach

To characterize the specific area of airborne nanostructured particles, a filter-based method of particle collection followed by gas adsorption analysis has been developed. Polycarbonate 0.4 µm pore-size filters cover all the required physical properties, specifically weight and surface stability under degassing conditions. Krypton gas was used as it is more suitable for low specific area measurement. Using this configuration, the instrument detection limit was established below 500 cm².

The proposed method is currently being validated on aerosols samples generated from commercial powders using a suitable generation bench (Fig. 1).

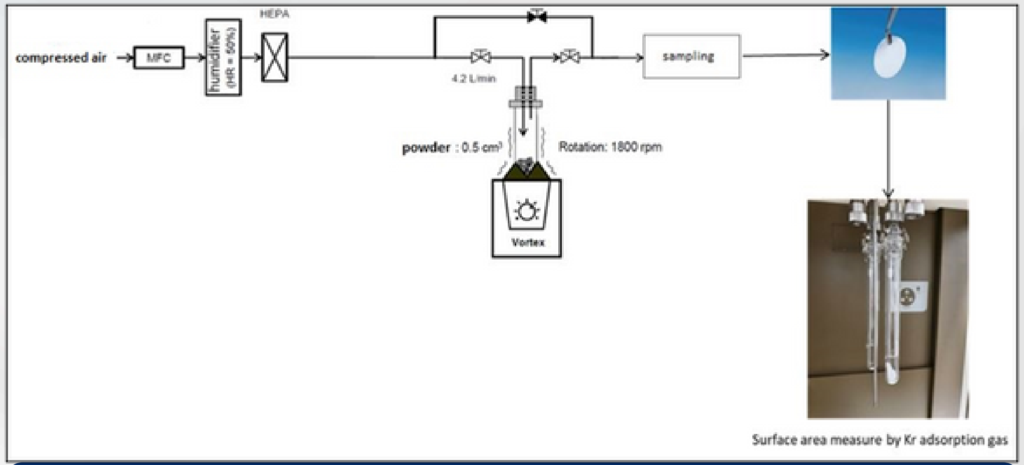


Diagram of the bench used to generate aerosol from commercial powders

Main results

Measurements were made on a mixture consisting of micron-sized particles (tile joint) and a nano silica powder (D10) added to improve the product's flowability. Due to the very different dustiness between the joint and the D10, the question arose whether the aerosol produced when handling the mixture would have the same characteristics as the initial powder. Comparison of the specific surfaces shows that the aerosol is richer in nanostructured particles. This observation reinforces the need to provide prevention officers with tools for characterizing aerosols, because studying the powder alone could lead to an operator's potential exposure being underestimated.

References

[1] Maynard A.D., Kuempel E.D. Airborne Nanostructured Particles and Occupational Health. J Nanopart Res, 7, 587–614 (2005).

[2] Stoeger T., Reinhard C., Takenaka S., Schroeppel A., Karg E., Ritter B., Heyder J., Schulz H. Instillation of six different ultrafine carbon particles indicates a surface area threshold dose for acute lung inflammation in mice. Environ Health Perspect, 114, 328-333

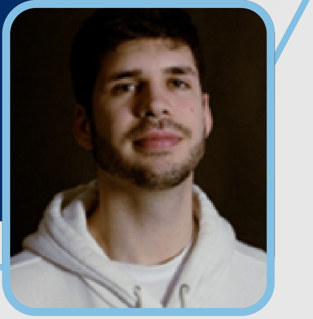
Metrology and methodology for analyzing risks related to exposure to natural stone dust

By Adrien Rizza, 2nd year

Supervisors: Dominique Thomas, Olivier Dufaud

Keywords

Dust stone | Exposure measurements | Security | Aerosol metrology



PERSEVAL, SAFE

General context, scientific issue

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.

Objectives and stakes

Natural stone dust often contains substances considered hazardous, such as crystalline silica [1]. The main objective of this work is to decrease the risks related to occupational exposure to dust stone by a) identifying new relationships between ambient concentration and employees exposure measurements, b) proposing new methods for mapping the dust emission as a function of the process.

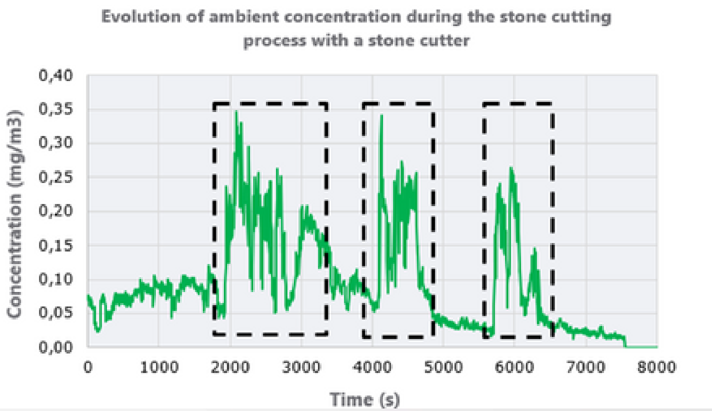
Methodology / Experimental approach

The methodology adopted to address the issue is as follows:

- 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.



Example of several stone cutting/stop cycles using a stone cutter.

Main results

The first year, visits to workshops and quarries provided an overview of natural stone shaping processes and also allowed the assessment of workers' exposure to this type of dust (Tufa stone, sandstone, limestone…). The second year of this work will be partially dedicated to the following points:

- The first part of my measurement campaign is completed, with winter measurements conducted in various companies working with different types of stone. A second part, scheduled for the summer, will begin in June. The objective is to compare the two seasons, which could serve as content for an article.
- Characterization of sensors used in ambient measurement is underway, to ensure their reliability for CFD simulations aimed at studying particle generation related to defined unit operations in marble processing.
- The assembly of a test bench is in progress. The objective will be to cut and sand stones to study the nature, shape, and concentrations of dust generated for the same operation on different types of stones. This will allow us to identify the most emissive stones, particularly by varying the moisture content of the stone.

References

[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.

Project HyBioT : Biofouling impact on heat transfer in cooling systems

Kevin Roudaut, research engineer

Supervisors: Nouceiba Adouani, Eric Olmos

Keywords

Heat exchangers | Biofilms | Biofouling | Experimental pilot | Hydrodynamics | Modeling

PERSEVAL, EDF

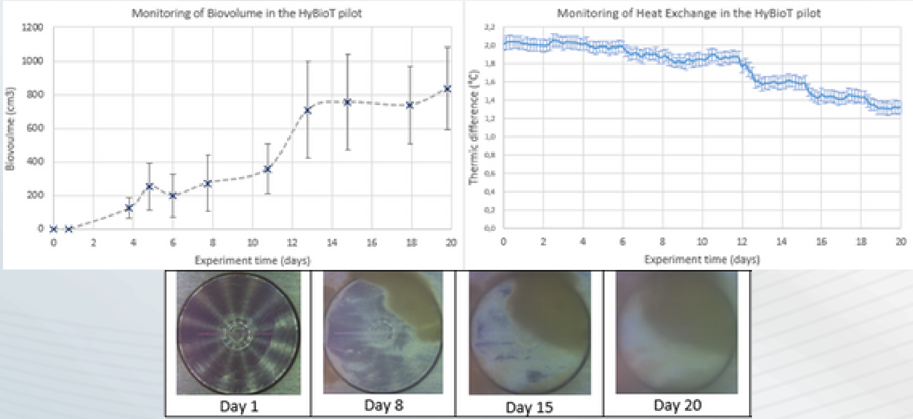
General context, scientific issue

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. Theses accumulations of matter, especially biofilms, reduce significantly the efficiency of heat transfer. Furthermore, biofouling can cause corrosion and biological pollution to receiving aquatic environments.

Methodology / Experimental approach

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 outcoming 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.



Title: 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

Several conditions (water temperature and flow) from the experimental design have been tested. The development of biofilm structures has been observed and their impact on heat exchanges are being quantified. It appears, as expected, that the reduction of thermic exchange is related to the biovolume (thickness associated with area of covering) and the structure of the biofilm developed.

Most of the anticipated assays have been performed and results indicate a difference in biofouling depending on experiment conditions. Indeed, in higher shear stress, partially due to biofilm detachment, it is less important. Furthermore, inlet water temperature appears to impact microbial growth in both suspended state and immobilized on biofilms. Those parameters influence microbiological composition and physical parameters.

From the collected data, a mathematical model is being constructed in order to optimize cooling process, predict biofilm development and thermal efficiency loss and to adapt the settings to reduce this impact. It could also be used to determine the threshold of interference of biofouling to reduce biocides use.

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.

Dynamic modelling for incinerator supervision

By Lionel , 3rd year

Supervisors: François Lesage, Abderrazak Latifi

Keywords

Waste
Thermal treatment
Modelling
Simulation
Process supervision

PERSEVAL, SUEZ

General context, scientific issue

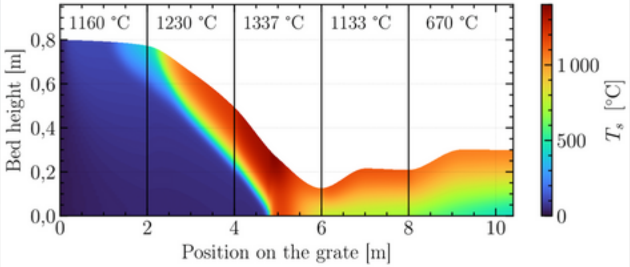
Incineration is a common waste disposal technique, thanks to its versatility, volume reduction capability and the energy recovered. Despite its overall simplicity and robustness, the heterogeneity of the waste and local phenomena make it a process hard to model and control.

Objectives and stakes

The essence of this research project consists in modelling the main process of an incinerator, 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, the conduct, and the maintenance of the incinerator.

Methodology / Experimental approach

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 media 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.



Solid temperature distribution of a simulated waste bed. The grate and primary air injection parameters are taken from the incinerator of Guichainville (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 contracting variant of the finite volumes and the so-called "walking-columns" approach. The 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 produced 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 computer program developed can produce waste bed representations (see illustration) and combustion outputs including dynamic responses with calculation times well under real time. The boiler is modelled using direct exchange surfaces and the thermal radiation zonal method. Both models are coupled through successive iterations. The global model provides insights on the behaviour of the waste kiln.

References

[1] E. Magnanelli, O. L. Tranås, P. Carlsson, J. Mosby, and M. Becidan, "Dynamic modeling of municipal solid waste incineration," Energy, vol. 209, p. 118426, Oct. 2020, doi: 10.1016/j.energy.2020.118426.

[2] Y. B. Yang, Y. R. Goh, R. Zakaria, V. Nasserzadeh, and J. Swithenbank, "Mathematical modelling of MSW incineration on a travelling bed," Waste Management, vol. 22, no. 4, pp. 369–380, Jul. 2002, doi: 10.1016/S0956-053X(02)00019-3.

[3] L. Meraz, A. Dominguez, I. Kornhauser, and F. Rojas, "A thermochemical concept-based equation to estimate waste combustion enthalpy from elemental composition," Fuel, vol. 82, no. 12, pp. 1499–1507, Aug. 2003, doi: 10.1016/S0016-2361(03)00075-9.

Dust explosion modeling: application to organic/mineral powder mixtures

By José Serrano, 3rd year

Supervisors: Olivier Dufaud, Laurent Perrin

Keywords

Dust explosion | ATEX | Powdermixture | Animal feed | Process safety | Risk assessment

PERSEVAL, TECALIMAN

General context, scientific issue

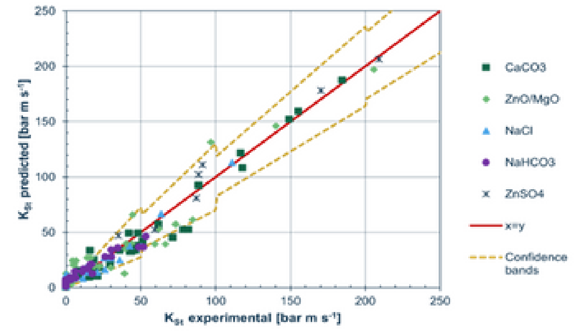
Explosion risk assessment in the animal feed industry is challenging due to the complex formulations and diverse physicochemical properties of powder mixtures known as premixes. Determining their safety parameters requires experimental tests that are both time-consuming and cost-inefficient.

Methodology / Experimental approach

Twelve organic and mineral powders were selected, considering their physicochemical properties and industrial relevance. These included combustible products such as cereals (e.g., Wheat middlings), vitamins (e.g., Vitamin E), and amino acids (e.g., Methionine). On the other hand, minerals such as sodium chloride (NaCl), calcium carbonate (CaCO3), and sodium bicarbonate (NaHCO3) were selected based on their inerting mechanism and efficiency.

The MIE, Pmax, and KSt parameters were determined using the MIKE3 and the 20-L sphere equipment following the ISO/IEC 80079-20-2:2016 standard. The experimental campaign involved extensive parametric study (366 tests) following Full Factorial and Box-Behnken Designs of Experiments. Subsequently, predictive models were built considering the significant factors found, comprising the chemical nature and particle size of the mineral powder, as well as the mass fraction and the respective safety parameter adjusted by the particle size of the organic powder.

Differential Scanning Calorimetry (DSC) and Micro Gas Chromatography (µ-GC) techniques have also been carried out to characterize the thermal behavior and identify explosion combustion gases.



Comparison between experimental and predicted KSt of organic/mineral powder mixtures

Objectives and stakes

This research addresses the development of a model to predict the ignition likelihood (Minimum Ignition Energy – MIE) and explosion severity (maximum explosion overpressure – Pmax and deflagration index – KSt) parameters of organic/mineral powder complex mixtures commonly used in premixes manufacturing to improve the implementation of optimal prevention and protection measures while considering inherently safety principles in the animal feed industry.

Main results

The particle size of both organic and mineral powders is a significant factor in determining the mixture's MIE because of its direct impact on the particle's heating time [1] and dust cloud homogeneity [2]. Nevertheless, this factor is less significant for predicting the Pmax and KSt parameters, as the particles fragmented during the dust cloud generation within the 20-L sphere [3]. Additionally, the safety parameters vary along the mixture's organic mass fraction, following non-linear trends beyond a certain threshold, depending on the chemical nature of the inert particles and the ignitability and explosibility of the organic dust.

The developed models are consistent with the experimental data, as previously illustrated, and aid in classifying complex powder mixtures according to their explosion safety parameters through proper control banding. Consequently, this approach facilitates the selection of optimal preventive and protective measures based on the mixture's formulation. Ongoing research focuses on establishing a phenomenological correlation with the collected data.

References

[1] N. S. Reding and M. B. Shiflett, "Characterization of Thermal Stability and Heat Absorption for Suppressant Agent/Combustible Dust Mixtures via Thermogravimetric Analysis/Differential Scanning Calorimetry," Ind Eng Chem Res, vol. 58, no. 11, pp. 4674–4687, Mar. 2019, doi: 10.1021/acs.iecr.8b06143.

[2] A. Janès, A. Vignes, O. Dufaud, and D. Carson, "Experimental investigation of the influence of inert solids on ignition sensitivity of organic powders," Process Safety and Environmental Protection, vol. 92, no. 4, pp. 311–323, Jul. 2014, doi: 10.1016/j.psep.2014.04.008.

[3] J. Serrano, A. Nowicki, L. Perrin, and O. Dufaud, "Effect of Particle Size Distribution and Inerting Mechanism on Explosion Severity of Organic/Mineral Mixtures," Chem Eng Trans, vol. 104, pp. 55–60, 2023, doi: 10.3303/CET23104010.

Comparative evaluation of the potential recovery of strategic metals (Co) from old mine tailings

By Samuel Teillaud, 3nd year

Supervisors: Lucie Coudert, Marie-Odile Simonnot, Marie Guittonny, Baptiste Laubie

Keywords

Mine tailings repurposing
Cobalt
Mineral processing
Agromining
Metal(loid) extraction
Hydrometallurgy
Residues stability

PERSEVAL, RIME

General context, scientific issue

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 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 recovery) and compared (in terms of Co and As pre-concentration efficiency, stability of final residue and operating costs, etc.).

Methodology / Experimental approach

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.

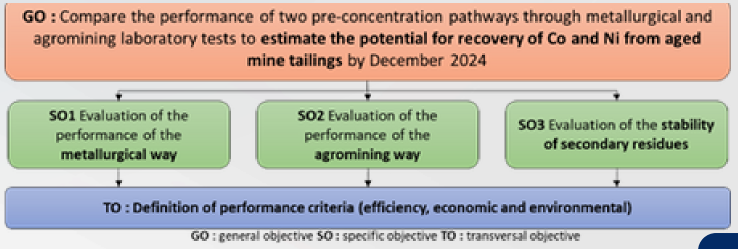
The laboratory work involved the use of various mineral processing separation processes, either combined or separately (e.g., gravity separation, size separation and flotation), sometimes preceded by pre-treatment steps (i.e., attrition, sonication) to reactivate minerals' surface or increase the liberation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

Additionally, laboratory work focusing on the preconcentration of Co using hyperaccumulating plants have been 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, were mixed with the residues, and cultivation trials were conducted under different conditions.

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/0.1007/978-3-030-58904-2_3



GO : Compare the performance of two pre-concentration pathways through metallurgical and agromining laboratory tests to **estimate the potential for recovery of Co and Ni from aged mine tailings** by December 2024

SO1 Evaluation of the performance of the **metallurgical way**

SO2 Evaluation of the performance of the **agromining way**

SO3 Evaluation of the **stability of secondary residues**

TO : Definition of performance criteria (efficiency, economic and environmental)

GO : general objective SO : specific objective TO : transversal objective

Project objectives

Main results

The physico-chemical characterization showed that the selected mine residues were mainly composed of fine particles (D80 = 55 µm) and contained 1310 mg/kg of Co and 5245 mg/kg of 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.

Flotation tests showed that the preconcentration of Co-bearing minerals is quite difficult (preconcentration factor of 1.2 to 2.5, recovery of 20 to 70%), while As-bearing minerals were a little bit more concentrated (preconcentration factor of 1.2 to 3.0, recovery of 25 to 80%). Sonication as a pretreatment step significantly enhanced the concentrations of Co- and As-bearing minerals through subsequent flotation. However, substantial hydrodynamic entrainment was observed, primarily attributable to particle size and the use of a Denver flotation cell, highlighting the specific challenges associated with this separation technique. The effectiveness of the flotation in separating targeted minerals from silicate gangue remained quite low, which can be explained by the complex mineralogy of mine tailings and hydrodynamic behavior 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.

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 and understand the underlying issues further.

Modelling and simulation of anoxic reactors in wastewater treatment plants - Application to micropollutant removal

By David Vauris, 1st year

Supervisors: Olivier Potier, Nouceiba Adouani

Keywords Hydrodynamics Computational Fluid Dynamics Activated sludge Residence Time Distribution Modelling Simulation Compartmental approach

PERSEVAL

General context, scientific issue

Several issues of concern require a deeper study on the existing and future wastewater treatment plants. For example, we can find the removal of micropollutants as a matter of health safety, energy that needs to be saved and water stresses increasing the concentration of pollutants in rivers.

Objectives and stakes

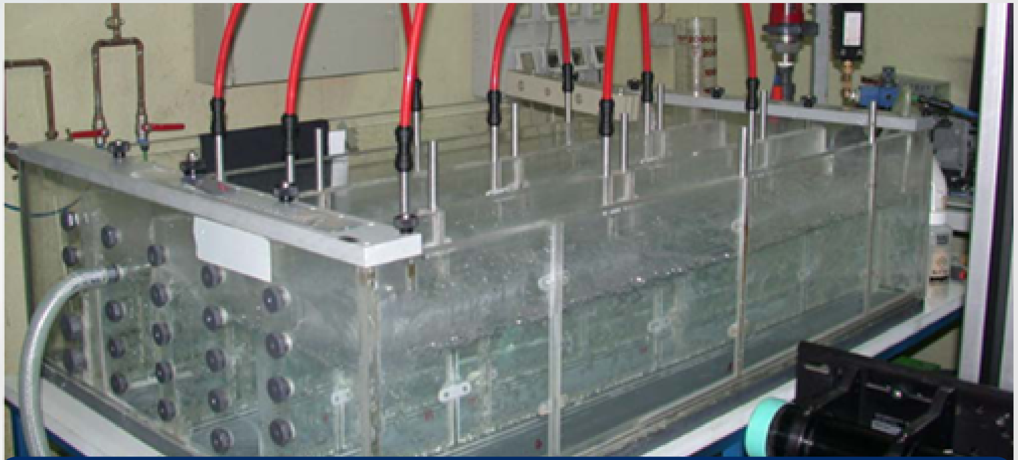
This work is focusing on the optimization of activated sludge anoxic reactors in order to improve their efficiency. Indeed, we look to better understand and model the hydrodynamics and to find better design of reactor, better location of internal elements (stirrer…) for a better global depollution.

Methodology / Experimental approach

This project is divided into three complementary parts. In the first part, as there are many shapes, sizes and proportions of activated sludge anoxic reactors that exist, we study the hydrodynamics of each of the main existing families of these reactors by using Computational Fluid Dynamics. These simulations will allow the visualization of velocity fields inside the reactors and will be able to give an overview of the Residence Time Distribution by using numerical tracing.

In the second part, some of these numerical experiments will be reproduced in the lab or on full-scale plants in order to validate the simulations by using experimental Residence Time Distribution and Particle Image Velocimetry as a comparison of the numerical values that were previously obtained.

Third: Modelling (see expected results)



Experimental pilot plant

Main results

As the PhD started in November 2023, there are no results yet, but all of these experiments should lead to the development of mathematical models representing the hydrodynamics in anoxic reactors and also the building of a compartmental model to simulate at lower computational cost the reactors of interest.
The better understanding of these reactors will help to optimize their design and improve their efficiency in terms of micro- and macro-pollutants removal and energy saving.

References

[1] Jourdan N., Neveux T., Potier O., Kanniche M., Wicks J., Nopens I., Le Moullec Y., 2019, Compartmental Modelling in chemical engineering: A critical review, Chemical Engineering Science, 210, 115196.
[2] Karpinska A.M., Bridgeman J., 2016, CFD-aided modelling of activated sludge systems-A critical review, Water Research, 88, 861-87.
[3] Wicklein E., Batstone D., Ducoste J., Laurent J., Griborio A., Wicks J., Saunders S., Samstag R., Potier O., Nopens I., 2015 Good Modelling Practice in Applying Computational Fluid Dynamics for WWTP Modelling, Water Science & Technology 73 (5), 969-98

Direct hybridization of a hydrogen fuel cell by batteries for a versatile, low energy suburban transport (HY2vers)

By Mengxi Wen, 2nd year

Supervisors: François Lapicque, Stéphane Rael

Keywords Proton Exchange Membrane Fuel Cell (PEMFC) Lithium-ion battery Direct hybridization Electric vehicles Suburban transport

PERSEVAL

General context, scientific issue

Electric vehicles, either battery- or fuel-cell-powered, are a possible solution for a sustainable future due to their zero-emission characteristics. However, current commercial electric passenger cars tend to be heavy, expensive, and too powerful in most cases, making them unsuitable for a wide range of urban and suburban personal transportation applications (with a maximum power demand of 30 W/kg [1]).

Methodology / Experimental approach

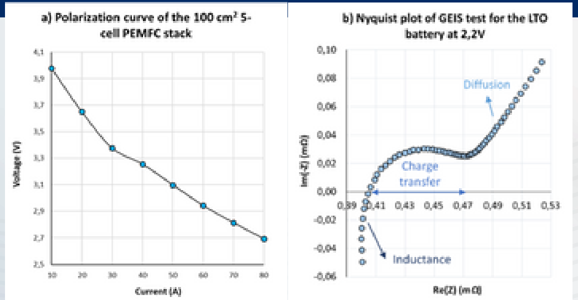
The thesis work will be conducted in two parallel parts: sizing and experimentation.

1. Hybrid source sizing

Firstly, the PEMFC stack and lithium-ion batteries (LIB) with different technologies (such as Lithium Iron Phosphate (LFP) and Lithium Titanate Oxide (LTO)) are characterized using a range of techniques to obtain their electrochemical parameters. These parameters are used to construct electrochemical models. Based on the established models, the operation of the hybrid source is simulated in Matlab and Simulink to determine its characteristics, such as its performance and its flexibility in powering a fictitious vehicle in urban and suburban driving conditions (e.g. New European Driving Cycle).

2. Experimentation

Meanwhile, hybridization experiments will be performed on the test bench to simulate the power distribution within the prototype hybrid source, initially on a small scale (FC ≈ 200 W) and subsequently on a larger scale (FC ≈ 2.5 kW). The comparison of experimental data and simulation results will help to refine certain parameters and modify some model assumptions.



Title: Characterization curves of a. the PEMFC stack and b. the lithium-ion battery for illustration

Objectives and stakes

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 (LIB) as the powertrain system for a lighter and cheaper electric vehicle dedicated to urban and suburban transportation. Indeed, 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.

Main results

A 100 cm2 5-cell PEMFC stack is first evaluated through Electrochemical Impedance Spectroscopy (EIS) to validate its performance, followed by polarization characterization (as exemplified in Illustration a). And a lithium-ion battery with Lithium Titanate Oxide (LTO) technology is characterized by charge-discharge tests and EIS tests (as exemplified in Illustration b).

Next, a polarization characteristic model is constructed for the fuel cell. Meanwhile, a model based on the Single Particle Model (SPM) with an improvement of the solid diffusion part is proposed for the Li-ion battery in order to reduce the possible computational errors for further applications.

The polarization characteristics of the FC and the electrochemical parameters of the LIB will then be used in the already existing models in Matlab and Simulink. In addition, hybridization tests will soon be performed on the test bench.

References

[1] C. Bonnet et al., "Direct fuel cell—supercapacitor hybrid power source for personal suburban transport," AIMSE, vol. 9, no. 6, pp. 1274–1298, 2021, doi: 10.3934/energy.2021059.

[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.

Impact of NOx on CO2 capture process by Pressure Swing Adsorption (PSA)

By Abas Woupndounou, Design Engineer

Supervisor: Léa Sigot

Keywords

Gas separation · Pressure swing adsorption · CO2 capture · NOx

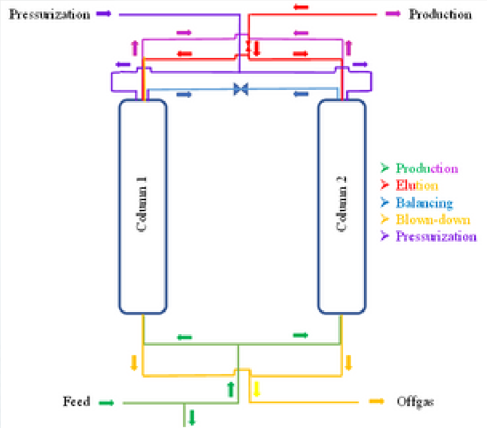
PERSEVAL, AIR LIQUIDE

General context, scientific issue

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 mature, its operation in presence of impurities such as NOx remains unexplored. In our study, we focus on the impact of these impurities on CO2 capture.

Methodology / Experimental approach

The project began with the design and installation of a semi-automated test bench to perform PSA cycles [2]. 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 bench is equipped with two columns for quasi-continuous gas separation. Dynamic parameters such as pressure, temperature, flowrates and compositions are monitored in real time by several sensors and transmitted to a control screen. Procedures have been established to ensure the pilot operation in safe conditions. The second part of this project consists in simulating different gas compositions to study several process indicators able to quantify the adsorbent performance to capture CO2 mixed with NOx. For each composition, a synthetic gas mixture is generated and the pilot has to be operated until steady state is reached. Monitored data post-processing enable to perform mass balances and to compare the behavior of the process.



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

Objectives and stakes

LRGP and Air Liquide are jointly conducting a study on CO2 capture in the presence of impurities. The aim of this study is to experimentally characterize the behavior of NOx in a PSA process designed for CO2 capture, with the ultimate goal of developing a model for process simulation. After conceptualization, assembly and installation of the lab-scale pilot, experimental designs were set up in order to acquire a wide range of data for a better understanding of the process.

Main results

The project is highly confidential; consequently, the technical details, materials, results and detailed process scheme could not be disclosed.

Following qualification and validation of the PSA process on binary gas mixtures (CO2/N2), tests were carried out introducing NOx. Experiments are now ongoing with different NOx concentrations according to the plan defined with Air Liquide.
It should be remembered that the tests are carried out according to predefined experimental designs, with fixed parameters such as pressure, residence time and flowrates. Accurate process indicator analysis enable to compare the impact of gas composition on the process performance in order to develop a reliable large-scale post-combustion CO2 capture solution. Beyond engineering stakes, it is about understanding the NOx behavior in the PSA process underlying adsorption mechanisms.

References

[1] Truc A. et al., Chem. Eng. J. 2020, 45:205-210.

[2] 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 May.21, 2024)[LS1]

[LS1]mettre à jour la date de consultation

Development of a novel hydrometallurgical process to recover zinc from vegetation for soil remediation

By Wen Xuan, ATER

Supervisors: Baptiste Laubie, Marie-Odile Simonnot

Keywords

Agromining · Zinc · Hyperaccumulator · Hydrometallurgy · Combustion · Alkaline leaching

PERSEVAL

General context, scientific issue

The intensification of industrial and agricultural activities throughout the 20th century led to a significant increase in zinc (Zn) concentrations in soils. Through phytoextraction, it is now possible to recover Zn from Noccaea caerulescens, recognized for their exceptional hyperaccumulation capacities (Hu et al., 2015; Reeves et al., 2001). An innovative hydrometallurgical process is being developed to recover Zn from N. caerulescens.

Methodology / Experimental approach

Between 2021 and 2022, several field campaigns were carried out in the north-eastern quarter of France in a context of Zn agromining. The robustness of the Zn recovery process was evaluated for different cultivation methods and populations of N. caerulescens. Initially, the hydrometallurgical process was rigorously applied for each batch of biomass harvested.

The results of this study revealed that one of the populations of N. caerulescens, native to the Vosges massif, accumulated the most Zn. Subsequently, this population was selected to continue the development of the Zn recovery process.

The sample was ground and dried before combustion. The ashes were washed with water at room temperature several times to remove potassium. Leaching in alkaline medium demonstrated better selectivity compared to acidic leaching. After alkaline leaching, almost all of the Zn contained in the leachate can be precipitated after increasing the pH by adding nitric acid. The remaining potassium and sodium can be removed by water leaching. Further purification with ammonium solution and ammonium chloride is in progress.

La Brassicacée Noccaea caerulescens. (De Muynck et al., 2015)

Objectives and stakes

A preliminary hydrometallurgical process has already been developed by the team to recover Zn and cadmium (Cd). The process involves combustion of biomass, water leaching, drying, leaching, cementation, precipitation and filtration (Hazotte et al., 2017). This project aims to validate the process with the samples from a harvest campaign performed by the laboratory of soil and environment (LSE) in 2022 in the vicinity of Lille, northern France. The new sample contains little Cd.

Main results

A zinc product was obtained from the harvested N. caerulescens through this process. The product also contains sodium (Na), potassium (K), aluminum (Al) and silicon (Si). After washing, the Na content can be lowered significantly, but the Al and Si are concentrated in the precipitateFurther purification with ammoniac and ammonium chloride solution is in progress.

References

[1] Hazotte C., Laubie B., Rees F., Morel J.L., Simonnot M.O. A novel process to recover cadmium and zinc from the hyperaccumulator plant Noccaea caerulescens. Hydrometallurgy, 2017, 174, p. 56-65.

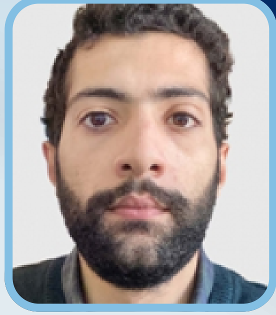
[2] Hu, P., Wang, Y., Przybyłowicz, W.J., Li, Z., Barnabas, A., Wu, L., Luo, Y., Mesjasz-Przybyłowicz, J., 2015. Elemental distribution by cryo-micro-PIXE in the zinc and cadmium hyperaccumulator Sedum plumbizincicola grown naturally. Plant and Soil 388, 267–282.

[3] Reeves, R.D., Schwartz, C., Morel, J.L., Edmondson, J., 2001. Distribution and Metal-Accumulating Behavior of Thlaspi caerulescens and Associated Metallophytes in France. Int. J. Phytorem. 3, 145–172.

[4] S. De Muynck, S. Kampelmann, A. Francioso, T. Drouet, et N. Noret, La phytoremédiation au service du développement durable. 2015.

PRIMO

Processes, Reactors, Intensification, Membranes, Optimization



CFD simulation of hydrodynamics and heat/mass transfer phenomena in membrane gas separation process

By Omar Abdul Majid, 3rd year

Supervisors: Rainier Hreiz, Eric Favre

Keywords CFD (computational fluid dynamics) Hydrodynamics Membrane separation Heat transfer Mass transfer

PRIMO

General context, scientific issue

Gas separation processes using membranes are gaining importance in industrial applications such as CO2 capture, natural gas purification, etc., 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.

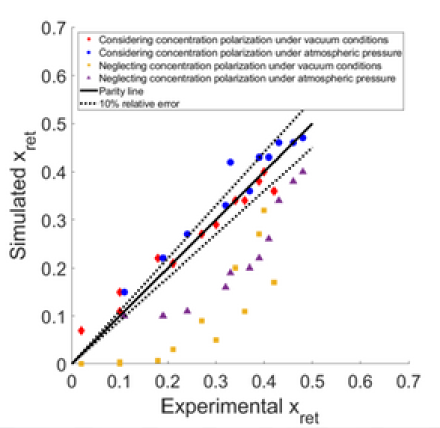
Methodology / Experimental approach

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 acquired on the gas permeation unit in the LRGP laboratory. After validation, the results of this model are compared with those of 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 modeling approaches.

This improved 1D model, is used to perform a cartography allowing 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.

Finally, the non-isothermal case that may occur in certain applications, mainly with high-pressure feed flows, will be studied and modelled with CFD, and if possible integrated to the improved 1D model to benefit from its reduced computational time and its user-friendly environment.



CO2 outlet mole fraction on the retentate side (xret): comparison of predictions for both models with experimental results for an equimolar feed mixture of CO2/CH4.

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].

Main results

Given the axial symmetry of the hollow fiber membrane problem, a 2D CFD model is developed to simulate the coupled transfer phenomena. 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 developed models are validated by a comparison of the predicted results with experimental results produced in the gas permeation unit of the LRGP laboratory. An exhaustive study on the impact of concentration polarization in membrane gas separation process is performed for two main applications, post-combustion CO2 capture and bio-gas purification.

A model that considers the effects of temperature change in gas separation using membranes is under development in order 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.

References

[1] W. J. Koros et C. Zhang, « Materials for next-generation molecularly selective synthetic membranes », Nat. Mater., vol. 16, no 3, Art. no 3, mars 2017, doi: 10.1038/nmat4805.

[2] E. Favre, « Chapter 2. Simulation of Polymeric Membrane Systems for CO2 Capture », 2011, p. 29-57. doi: 10.1039/9781849733472-00029.

[3] R. B. Bird, W. E. Stewart, et E. N. Lightfoot, Transport phenomena, Revised second edition. New York: John Wiley & Sons, Inc., 2007. Consulté le: 15 février 2023. [En ligne]. Disponible sur: http://www.ulb.tu-darmstadt.de/tocs/197301053.pdf

Hollow fiber membrane contactors for intensification of stripping operations: generic approach and application to water treatment

By Omar Aljasem Alhmiedy, 2nd year

Supervisors: Bouchra Belaissaoui, Sabine Rode

Keywords Hollow Fiber Membrane Contactor | Degassing | Stripping | Water Treatment | Modeling

PRIMO

General context, scientific issue

In industrial processes, the removal of low concentrations of volatile compounds in water is typically achieved through the use of vacuum, sweep gas, or a combination of the two. The stripping operation is typically achieved in packed columns. Hollow fiber membrane contactors (HFMC) offer both higher specific contact area and higher mass transfer coefficients. Nevertheless, pressure drop issues and inadequate fluid distribution in the liquid phase continue to present challenges in the design and optimization of HFMCs.

Objectives and stakes

The objective of this research is to develop a parsimonious yet rigorous modelling approach for the design of HFMCs for the stripping of volatile components from water. In order to provide a realistic estimate of system performance, the model must, on the one hand, integrate the residence time distribution of the liquid flow and, on the other hand, take into account the partial pressures of the stripped components on the gas side. In the existing literature, the liquid flow is always assumed to be an ideal plug flow, and the gas-side partial pressures of the stripped gases are always neglected. These assumptions often lead to inaccurate estimates of the mass transfer coefficient, which hampers the optimization of these systems.

Methodology / Experimental approach

In most commercial HFMCs used for stripping applications, the gas and the liquid are in cross-flow. The liquid is distributed through a perforated cylindrical central tube. It flows radially around the fibers and is evacuated at the periphery. A schematic representation of a commercial device using vacuum is shown in Fig. 1. To validate the developed modeling approach, experimental data on the stripping of dissolved oxygen from water in commercial modules were exploited (data provided by the supplier) considering ideal plug flow but realistic gas-side partial pressures. In the next step of the research work, the residence time distribution of the liquid phase will be characterized for different commercial contactors and different operating conditions.

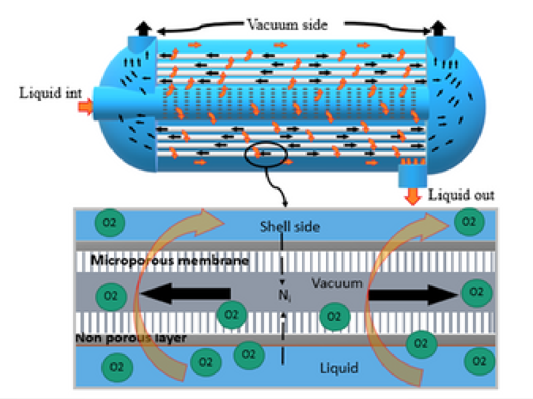


Figure 1. Schematic representation of liquid and gas flow through the module SEPAREL EF-series HFMC. The stripping of dissolved oxygen is illustrated

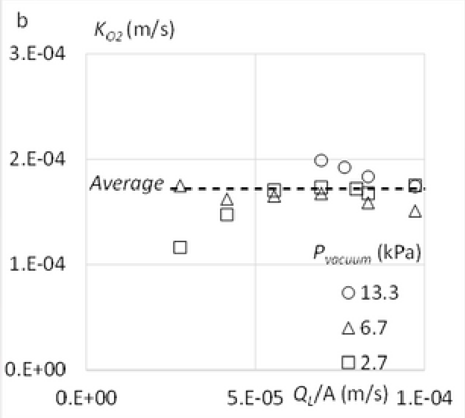


Figure 2. Mass transfer coefficient using the developed model in a commercial SEPAREL-EF HFMC working at oxygen recovery rates higher than 70%

Main results

As illustrated in Figure 2, the average mass transfer coefficient which characterizes a given HFMC module operating in conditions leading to high oxygen recovery rates, is independent of both the liquid flow rate and the applied vacuum pressure. This finding is consistent with the laminar liquid flow around the fibers, which leads for high recovery rates to a developed concentration profile on the shell-side.

References

Ghadiri, Mehdi, Azam Marjani, and Saeed Shirazian. 2013. "Mathematical Modeling and Simulation of CO2 Stripping from Monoethanolamine Solution Using Nano Porous Membrane Contactors." International Journal of Greenhouse Gas Control 13 (March): 1–8. https://doi.org/10.1016/j.ijggc.2012.11.030.

Comparative approach of flow chemistry and conventional reactor chemistry for optimal synthesis

By Francisco Eduardo Bolaños García, 1st year

Supervisors: Laurent Falk, Jean-Marc Commenge

Keywords Flow chemistry Optimization Chemical reactors Design of experiments

PRIMO, CEISAM

General context, scientific issue

Optimized conditions derived from flow chemistry platforms [1] are not directly applicable to conventional reactors (stirred, semi-batch or continuous), as the change of scale often results in a significant drop in yield and selectivity. This is because chemical reactions, mixing and heat and mass transfer between phases are governed by specific kinetics, each of which has its own dependence on the geometric dimension, but also on the type of reactor used.

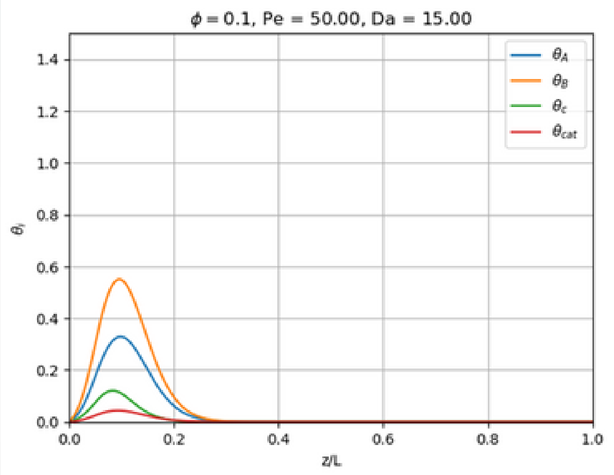
Objectives and stakes

Use the reaction model derived from the flow chemistry results for the development of an experimental strategy based on a more complex and complete model. Then, it will be necessary to develop and operate a platform of conventional and instrumented reactors (tubular reactors, stirred fed-batch and batch reactors) to optimize the synthesis conditions using this platform and compare the optimum obtained by flow chemistry.

Methodology / Experimental approach

A model-based design of experiments (MBDoE) [2] will be conducted to extract kinetic parameters from experiments performed in a flow chemistry platform operating under non-steady state conditions via the injection of a reactive volume. Once the model is derived, it will enable the prediction of optimal conditions for the flow platform, which will be compared with data-driven optimization results. This kinetics will be utilized to model stirred tank reactors and determine the impact of less efficient mass and heat transfer on the optimal conditions.

Initially, the methodology will be validated using a reaction with previously determined kinetic parameters. Then, it will be applied to a second reaction case where kinetics are unknown: the synthesis of benzopyrans through the condensation of phenols with α,β-unsaturated aldehydes. This transformation provides direct access to benzopyran structures, which constitute the core structure of numerous natural products, particularly cannabinoids widely employed in traditional Asian or African medicine for treating inflammation and pain.



1D simulation of an advection-diffusion model with reaction

Main results

The yield obtained from a flow reactor operating under non-steady state conditions with dispersion differs from that of a flow reactor in steady-state conditions. Achieving the same yield requires increasing the ratio between the volume of the injection pulse and the reactor volume.

Additionally, kinetic parameters can be extracted by fitting a 1D non-steady state model to experimental results and conducting an MBDoE to identify the next best batch of experiments, increasing the precision of the estimated parameters. The primary challenge lies in conducting the DoE online, as it requires multiple iterations in minimal time. Utilizing a 1D model for this purpose isn't optimal. Therefore, the option of employing an artificial neural network trained on the results of the knowledge-based model is being explored.

References

[1] Senthil Vel A. et al., Organic Process Research & Development, 2023
[2] Cenci F. et al., Comput. Chem. Eng., 2023, 177 :108353

Integration of Direct Air Capture (DAC) in a low-carbon system

By Paul de Joannis de Verclos, 2nd year

Supervisors: Christophe Castel, Olivier Authier, Eric Favre

Keywords Simulation Direct Air Capture Carbon Dioxide Removal Process DAC CO2

PRIMO, EDF

General context, scientific issue

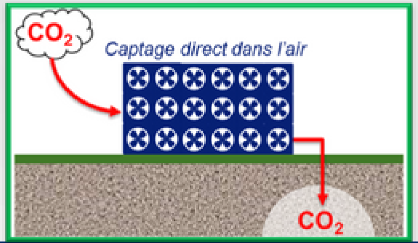
There has been a recent and growing interest in Direct Air Capture (DAC) technology because of its potential to decarbonize and achieve carbon neutrality. This negative emission technology captures CO2 from the atmosphere and then stored it almost permanently or converts it to valuable product.

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 perspectives, based on the main techniques for CO2 separation from ambient air through modelling and numerical simulation.

Methodology / Experimental approach

The approach involves first studying individual DAC technologies based on four separation techniques - absorption, adsorption, membrane, and electrochemistry - and then investigating the hybridization of these technologies to improve performance. These DAC processes will be studied at a commercial scale and for integration into a low-carbon energy production system. Modeling, simulation, and economic analysis will be used to assess overall and techno-economic performance.
Absorption using monoethanolamine [1] as a solvent under DAC conditions is evaluated by simulation in Aspen Plus. Adsorption is studied using the particle bed adsorbent "Lewatit VP OC 1065" and a yet-to-be-defined monolithic adsorbent simulated under dynamic mode in Aspen Adsorption. Membrane separations using PolyActive from Hereon are simulated using the MEMSIC tool [2]. An electrochemical process called “Electro-Swing Adsorption” [3] is studied under dynamic mode using MATLAB simulations. All processes will be economically evaluated using the Aspen Process Economic Analyzer tool. Finally, the hybridization of DAC technologies and their integration into a low-carbon energy production system will be assessed.



Remove CO2 from the atmosphere with Direct Air Capture

Main results

Main work has been done on DAC using monoethanolamine absorption with heat pump enhancements, such as Lean Vapor Compression (LVC) and Stripper Overhead Compression (SOC), to reduce reboiler requirements during regeneration. This process is modelled using Aspen Plus and incorporating the CCSI (Carbon Capture Simulation Initiative) model adapted and suited for DAC environmental conditions. Technical performance was investigated through a sensitivity analysis of various environmental and process parameters, including MEA emission, air inlet temperature and humidity, and factors such as solvent loading, capture rate, gas velocity, and liquid to gas ratio. A scrubber section above the absorber was installed to mitigate MEA emission. The implementation of LVC and SOC results in a 25% reduction in regeneration consumption compared to conventional MEA-based processes. However, due to additional capital investment, the capture cost is similar to that of the conventional process. Regulatory limits on MEA emission at the air outlet significantly impact the dimensions of the scrubber section and thus the overall capture cost, which decreases by 8% for a 6 ppm-mol limit compared to a 0.1 ppm-mol limit. Detailed techno-economic analyses were performed for design cases with capture scales ranging from 0.1 MtCO2/yr to 1 MtCO2/yr, with capture costs ranging from 1091 to 1283 €/tCO2.
The Electro-Swing Adsorption process was modeled and simulated in MATLAB with the assistance of an intern. Oxygen in the air may cause degradation of the electrode material (quinone) by oxidation.
Adsorption and membrane separation processes are under evaluation.

References

[1] A. Kiani, K. Jiang, et P. Feron, « Techno-Economic Assessment for CO2 Capture From Air Using a Conventional Liquid-Based Absorption Process », Frontiers in Energy Research, vol. 8, 2020, Consulté le: 3 novembre 2022. [En ligne]. Disponible sur: https://www.frontiersin.org/articles/10.3389/fenrg.2020.00092

[2] R. Bounaceur, E. Berger, M. Pfister, A. A. Ramirez Santos, et E. Favre, « Rigorous variable permeability modelling and process simulation for the design of polymeric membrane gas separation units: MEMSIC simulation tool », Journal of Membrane Science, vol. 523, p. 77-91, févr. 2017, doi: 10.1016/j.memsci.2016.09.011.

[3] S. Voskian et T. A. Hatton, « Faradaic electro-swing reactive adsorption for CO2 capture », Energy Environ. Sci., vol. 12, no 12, p. 3530-3547, déc. 2019, doi: 10.1039/C9EE02412C.

Geomaterial-based composite membranes for textile wastewater nanofiltration: fabrication, testing and process design

By Zakarya Chafiq Elidriss, 2nd year

Supervisors: Bouchra Belaissaoui, Sabine Rode, Mohamed Ouammou, Brahim Achiou

Keywords Geomaterials Ceramic membrane Membrane process Modeling Design Wastewater

PRIMO

General context, scientific issue

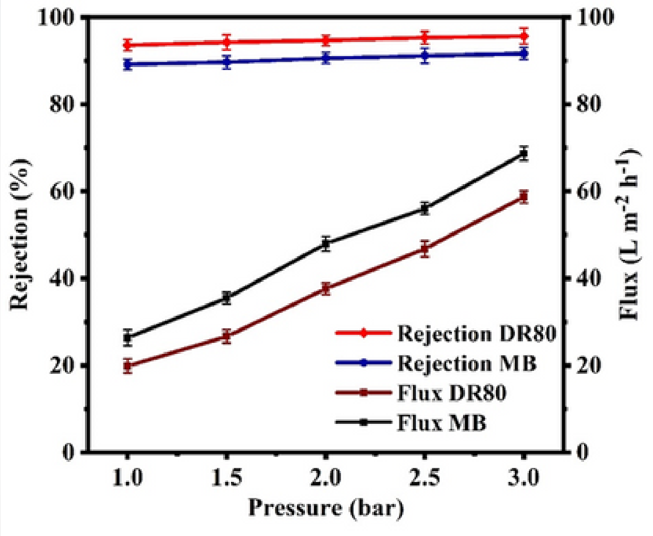
At a time when environmental issues are important, it is necessary to consider the production of membranes using ecological and natural raw materials with a green manufacturing process. Geomaterials-based ceramic membranes permit to overcome the impediment of the cost of ceramic membrane manufacturing. However, the cost/performance ratio remains challenging, especially for the fabrication of nanofiltration membranes. Nanofiltration (NF) is one of the most adopted technologies for removing textile dyes thanks to its low molecular weight cutoff and small pore size ranging from 0.5 to 2 nm.

Objectives and stakes

The separation performance of NF membranes is dependent on a number of factors, including the characteristics of the solutes (e.g. dye size, charge and concentration), the properties of the membrane (e.g. thickness and surface charge) and the operating conditions (e.g. feed pressure and flow rate). Various transport mechanisms may be involved, such as diffusion, convection, sieving effect and Donnan exclusion effect. Several models have been proposed to describe the nanofiltration process. Some models rely on simple concepts, while others require more sophisticated solution techniques. For the purpose of efficient and reliable process design and optimization, it is necessary to employ an adequate modelling strategy capable of accurately describing mass transport through NF membranes. This thesis aims to develop and characterize novel nanofiltration membranes based on geomaterial substrates for the removal and recovery of dyes from textile wastewater.

Methodology / Experimental approach

Firstly, a novel composite membrane based on molybdenum disulfide/cross-linked polyvinyl alcohol (MoS2/C-PVA) was developed. Secondly, membrane permeability and rejection of direct red 80 (DR80) and methylene blue (MB) under various operating conditions, including feed pressure, dye concentration, and ionic strength, were conducted using a laboratory cross-flow setup. The transport parameters of dyes through the prepared membranes were determined by fitting the experimental values with Spiegler-Kedem and film models. This will ultimately permit the quantification of the effectiveness of the new membranes and the comparison of their separation performances with those of existing nanofiltration membranes.



Permeate flux and rejection rate of MB and DR80 under different pressure values.

Main results

As illustrated in the accompanying diagram, the prepared membrane exhibits an exceptional ability to reject both dyes, thereby demonstrating its efficacy in the filtration process. The observed difference in rejection can be attributed to the charge, size, and molecular structure of the dyes, indicating that the filtration mechanism is primarily governed by the Donnan exclusion mechanism and sieving effect. The parameters of the Spiegler-Kedem and film models, namely solute permeability (Ps), reflection coefficient (σ), and mass transfer coefficient (k), were estimated by minimizing the error between experimental and calculated values.

References

[1] O. Agboola, J. Maree, A. Kolesnikov, R. Mbaya, and R. Sadiku, Environ. Chem. Lett. 2015, 13, 37 47.

Contribution of the P-graph framework for process-simulator-based optimization

By Darrick Hillaby, 1st year

Supervisors: Andrés Piña-Martinez, Jean-François Portha, Laurent Falk

Keywords P-graph Superstructure Process-simulator-based optimization Process synthesis

PRIMO

General context, scientific issue

Process Systems Engineering (PSE) is the development of systematic techniques for process modelling, design, control and optimization, i.e., process synthesis. The mathematically formulated problem is then solved with PSE software tools [1]. [ADPM1] Despite the technological advances made recently, these tools are still incapable to manage the constraints due to interdependent connections between operating units. P-graph framework however, provides a systematic and effective approach to process synthesis [2].

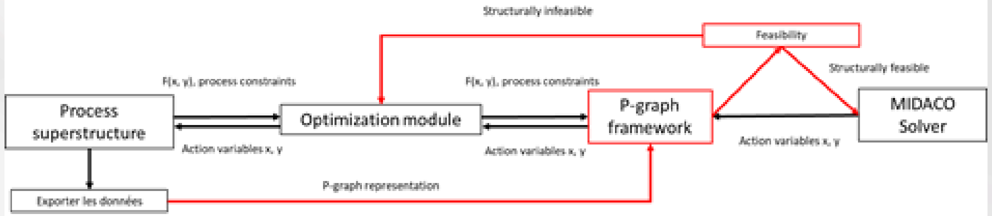
Methodology / Experimental approach

The novel methodology is determined by modifying the existing P-graph framework and improving the approach to suit users using ProSimPlus (PSP). However, optimization tools provided by typical commercial simulation packages are not as effective or flexible as needed due to the high nonlinearity of the equation systems. One proposed strategy to tackle this issue is using an evolutionary algorithm such as Ant Colony Optimization (ACO). MIDACO is effective for highly complex problems, since it is derivative-free [4]. [ADPM1] MIDACO combines an extended evolutionary ACO algorithm with the Oracle Penalty Method for constrained handling. Since MIDACO is a black-box solver, an interface between these two programs is needed.

The proposed methodology follows an iterative loop. To begin optimizing a process superstructure, the user defines the problem in PSP, specifying various alternatives of a chemical process interconnected with structural switches, the objective function, and process constraints. Once defined, the interface between PSP and MIDACO is invoked to run an algorithm, translating the process flowsheet from PSP into a matrix P-graph representation. This interface then calls MIDACO to assign the action variables. A modified P-graph framework algorithm assesses the structural feasibility of these action variables. If the structure is feasible, PSP runs the simulation and sends the objective function to MIDACO. If the structure is not feasible, the objective function is penalized and sent to MIDACO. Based on the objective function evaluation, a new set of action variables is provided by MIDACO.

Objectives and stakes

There are two process synthesis approaches: heuristics-and-decomposition based and optimization based [3]. The former relies on heuristics and may not yield optimal outcomes, while the latter provides a more refined solution. Thus, the optimization approach is preferred for designing modern processes. A key challenge in process synthesis is defining the structural constraints. Different processes have different structural constraints which complexifies the process synthesis problem. This thesis aims to tackle this issue by introducing a P-graph framework-based methodology to optimize process superstructures. Two specific objectives are studied: translating process simulator flowsheet to P-graph representation and reducing the optimization time.



A typical process-simulator based optimization with the methodology proposed in highlighted in red

Main results

The new method simplifies process optimization by avoiding many structural constraint equations that grow with problem complexity.

References

[1] E. N. Pistikopoulos et al., 'Process systems engineering – The generation next?', Comput. Chem. Eng., vol. 147, p. 107252, Apr. 2021, doi: 10.1016/j.compchemeng.2021.107252.
[2] F. Friedler, A. Orosz, and J. Pimentel Losada, P-graphs for Process Systems Engineering: Mathematical Models and Algorithms. Cham: Springer International Publishing, 2022. doi: 10.1007/978-3-030-92216-0.
[3] L. Mencarelli, Q. Chen, A. Pagot, and I. E. Grossmann, 'A review on superstructure optimization approaches in process system engineering', Comput. Chem. Eng., vol. 136, p. 106808, May 2020, doi: 10.1016/j.compchemeng.2020.106808.
[4] M. Schlueter and M. Munetomo, 'Introduction to MIDACO-SOLVER Software', Mar. 2013, Accessed: May 23, 2024. [Online]. Available: http://www.midaco-solver.com/data/other/MIDACO_User_Manual.pdf

Energetical analysis of a compression-separation membrane system

By Mathilde Lafont, 2nd year

Supervisors: Christophe Castel, Romain Privat

Keywords Membrane separation process | Simulation | Energy | Thermodynamics | Transitory state

PRIMO

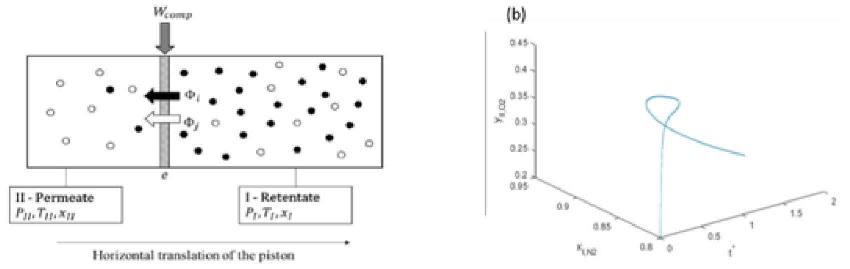
General context, scientific issue

Membrane separations are a key technology in gas separation, with an easy steady-state operation and a wide range of applications. However, the limitations can come from the materials available industrially, and it has been theorized [1] that operating under an unsteady state could increase separation performances and circumvent the issue.

Methodology / Experimental approach

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).

An experimental set-up was designed and built, aiming to test the reliability of the model created was the simulations. Using a precise translation stage the pressure is controlled during a first compression stage, and the retentate is the analyzed by gas chromatography. Obtaining experimentally the same pressure, temperature and composition path as what was simulated will constitute the first validation of the concept.



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

Objectives and stakes

Different possible implementations have been studied to enhance the efficiency of the process [2-4]. The objective of this research is to study an innovative implementation, using simultaneous compression-separation steps. It operates in an unsteady state and focus on energy consumption minimization. The concept is to use a piston compressor, with a modified head where a membrane is encased. A gas mixture to be purified is fed in one compartment and the progressive compression drives the separation.

Main results

A parametric study was conducted on the main dimensionless number obtained from the model: the permeation number, the thermal number and the selectivity. It showed the main variables influencing the membrane piston performances. The results obtained was compared to a steady-state system while keeping an identical pressure at the end of the separation. In some studied cases (air separation considering a binary mix of 80%N2/20%O2 or a mixture of 50%CO2/50%CH4), the unsteady state process showed similar performances for a targeted purity with less required work. The experimental set up was started recently and results are expected soon.

References

[1] Paul, D. R. Membrane Separation of Gases Using Steady Cyclic Operation. Ind. Eng. Chem. Process Des. Dev.10, 375–379 (1971).
[2] Trubyanov, M. M. et al. Unsteady-state membrane gas separation by novel pulsed retentate mode for improved membrane module performance: Modelling and experimental verification. J. Membr. Sci. 530, 53–64 (2017).
[3] Feng, X., Pan, C. Y. & Ivory, J. Pressure swing permeation: Novel process for gas separation by membranes. AIChE J. 46, 724–733 (2000).
[4] Wang, Lei. Séparation Membranaire de Composés Gazeux en Régime Cyclique. (Université de Lorraine, 2012).

Optimal design of reactor-exchangers through minimization of entropy generation

By Audrey Michaud, 2nd year

Supervisors: Jean-François Portha, Rainier Hreiz

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

PRIMO

General context, scientific issue

Improving processes' energy efficiency is one of the main challenges of our century, where the need to stop global warming requires preventing energy losses. Minimizing these losses, modelled by entropy generation, leads to optimal-shaped reactors that reduce energy consumption.

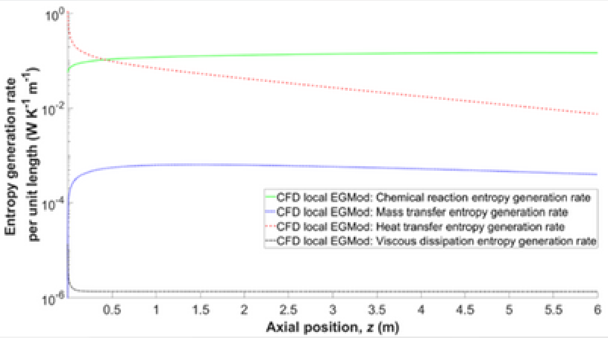
Objectives and stakes

The goal of this work is to model the entropy generation accurately first and then to use this entropy generation rate as an objective function, which, when minimized, provides a reactor with a design that minimized energy losses [1]. The methodology is applied to a heat exchanger plug flow reactor where the hydrolysis of acetic anhydride is carried out. This study is carried out using both a 1D systemic model and CFD simulations of the reactor and the results will be validated with experimental results [2].

Methodology / Experimental approach

There are two commonly used entropy generation modelling approaches. The first one is a global approach, corresponding to an entropy balance, which allows for the calculation of entropy generation through an entropy balance over the system boundaries. This method is not computationally demanding but offers little insight into the sources of entropy generation inside the system. On the other hand, local modelling of entropy generation [3-4], based on local non-equilibrium thermodynamics, offers the possibility to qualitatively and quantitatively assess the entropy production but is computationally more demanding.

These entropy generation modelling approaches were applied to two process models. The first one is a 1D systemic model, and the second one is a 2D CFD model. The accuracy of each process model and entropy generation approach is discussed. Using the results given by the entropy generation modelling assessment, the geometrical optimization of the heat exchanger reactor is conducted to find the optimal diameter profile of the system. These results will be compared to experimental data in order to validate the methodology.



Axial profiles of the local entropy sources (per unit length) calculated using the CFD local EGMod approach

Main results

Both local and global entropy modelling approaches were applied to the systemic and CFD process models. Four main sources of entropy were modelled:
·Viscous dissipation, driven by pressure gradients
·Heat transfer, occurring with temperature inhomogeneities
·Mass transfer, represented by gradients of chemical potentials
·Chemical reaction, arising from non-zero chemical affinity
It was shown that, for each system model, the global and local approaches lead to similar results and chemical reaction was found to constitute the main source of entropy generation in the system. Additionally, it was demonstrated that, between the 1D and 2D/3D system models, there was a good agreement for viscous dissipation and heat transfer entropy generation, but the 1D systemic model was proven to be insufficient for accurately modelling the entropy generation due to the chemical reaction. This inadequacy arises from the strong coupling between local temperatures and concentrations, which a 1D systemic model cannot adequately reflect, even if averaged temperature and concentration profiles are accurately predicted.

References

[1] Bejan, A. « Entropy generation minimization: the method of thermodynamic optimization of finite-size systems and finite-time processes». CRC Press, 1996.
[2] Ferrasse, J-H. « NACREE : Nouvelle Approche des Convertisseurs Réactifs par Équipartition de la production d'Entropie », 2021
[3] Johannessen, E. « Minimum Entropy Production Rate in Plug Flow Reactors: An Optimal Control Problem Solved for SO2 Oxidation ». Energy, vol. 29, no 12-15, décembre 2004, p. 2403-23. DOI.org (Crossref), https://doi.org/10.1016/j.energy.2004.03.033.
[4] Sciacovelli, A., & al. « Entropy Generation Analysis as a Design Tool—A Review ». Renewable and Sustainable Energy Reviews, vol. 43, 2015, p. 1167-81. DOI.org (Crossref), https://doi.org/10.1016/j.rser.2014.11.104

Methodology for systematic process design: analysis of superstructural and generative approaches

By Antonio Rocha Azevedo, 2nd year

Supervisors: Jean-Marc Commenge, Romain Privat

Keywords Process synthesis · Process Systems Engineering · Superstructure · Generative approaches · Optimization

PRIMO, EDF

General context, scientific issue

Process synthesis describes the search for optimal process conception (i.e., determination of optimal flowsheet and corresponding operating conditions). Two classes of 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.

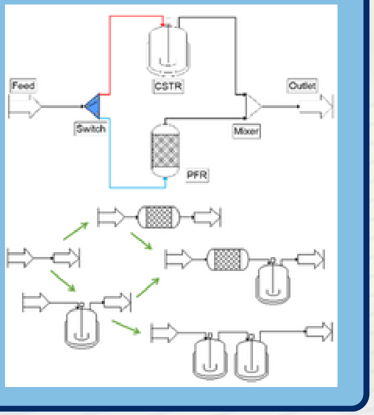
Objectives and stakes

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 / Experimental approach

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. The definition of the superstructure is a key question that must be addressed first. A process simulator is used for implementation of the superstructure, and optimization is done through a direct-search algorithm. Although superstructures allow for the simultaneous optimization of both the structure and continuous variables, this method can only determine the optimal structure contained in the superstructure.

To get around this limitation, generative approaches – not limiting 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 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 [4].



Superstructural vs evolutionary approach

Main results

The design of supercritical CO2 Brayton cycles has been picked as a first application for comparison of synthesis approaches since superstructural optimization results were readily available [5]. Dealing with infeasibilities has been a challenge: generative approaches may propose structures that bypass modelling safe-guards, yielding processes that are artificially good, but are in practice non-physical ; spoiling results. Furthermore, improving the computational efficiency of these approaches has been a necessity. A stabler version of the simulator used has allowed the evolutionary approach to yield promising results: it manages to reproduce multiple heuristics of the application, although results are not quite at the level of the superstructural approach. Next, Machine Learning methods will be compared, before a new application is picked for new analysis including more complex considerations (e.g., modelling approaches and uncertainty).

References

[1] Neveux, T., Addis, B., Castel, C., Piccialli, V., & Favre, E. (2022). A comparison of process synthesis approaches for multistage separation processes by gas permeation. In L. Montastruc & S. Negny (Eds.), Computer Aided Chemical Engineering (Vol. 51, pp. 685–690). Elsevier. https://www.sciencedirect.com/science/article/pii/B9780323958790501156

[2] Nabil, T., Commenge, J.-M., & Neveux, T. (2022). Generative Approaches for the Synthesis of Process Structures. In Y. Yamashita & M. Kano (Eds.), Computer Aided Chemical Engineering (Vol. 49, pp. 289–294). Elsevier. https://www.sciencedirect.com/science/article/pii/B9780323851596500488

[3] Neveux, T. (2018). Ab-initio process synthesis using evolutionary programming. Chemical Engineering Science, 185, 209–221. https://doi.org/10.1016/j.ces.2018.04.015

[4] Nabil, T., Le Moullec, Y., & Le Coz, A. (2019, September 19). Machine Learning Based Design of a Supercritical CO2 Concentrating Solar Power Plant. 3rd European supercritical CO2 Conference, Paris, France. https://doi.org/https://doi.org/10.17185/duepublico/48885

[5] Zhao, Q., Mecheri, M., Neveux, T., Privat, R., Jaubert, J.-N., & Le Moullec, Y. (2023). Search for the Optimal Design of a Supercritical-CO2 Brayton Power Cycle from a Superstructure-Based Approach Implemented in a Commercial Simulation Software. Energies, 16(14), 5470. https://doi.org/10.3390/en16145470

Study and optimization of a micro-CHP process with integration of intensified heat-exchanger/reactors

By Di Wu, 4th year

Supervisors: Jean-Marc Commenge, Laurent Falk

Keywords

Micro-Combined Heat and Power
Process intensification
Multicriteria optimization
Fuel partialization

PRIMO, AUER

General context, scientific issue

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.

Objectives and stakes

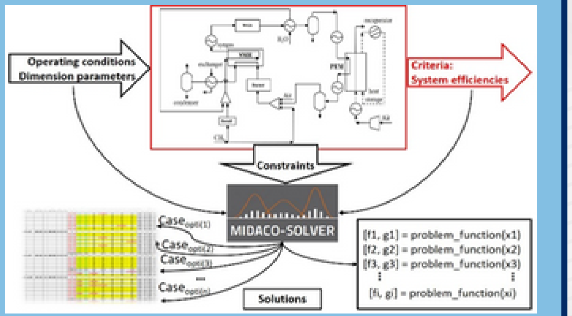
The main objective of this study is to develop a μ-CHP process based on the fuel cell with the integration of a millistructured reactor-exchanger. In this context, the approach aimed firstly to build a compact reactor-exchanger model, and then to integrate the model into the complete process. Finally,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

Methodology / Experimental approach

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.

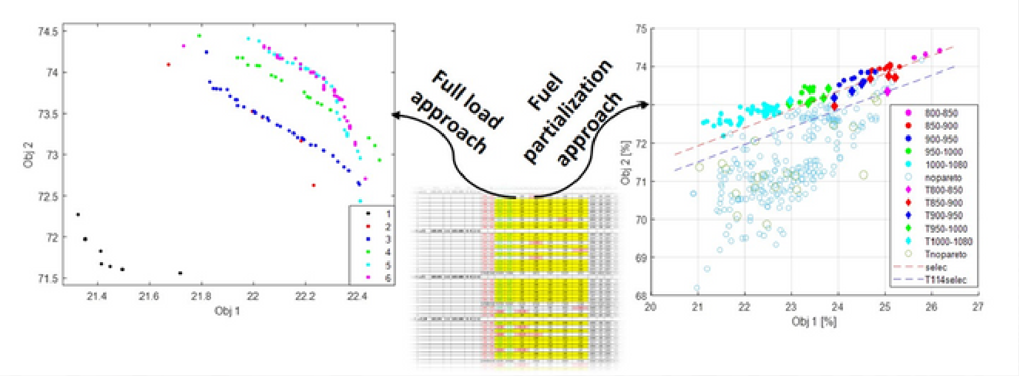
The data was analyzed in the domain of decision variables to identify the optimum operating conditions at fixed power, as well as the modulation strategies required to provide continuously optimal behavior under variable electrical power conditions.



System optimization construction

Main results

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 other 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 optimality fronts obtained from the latter have been determined by using a linear function. The result shows higher level of compatibility for higher values of electrical power with the complete optimization case study (diamond points).



References

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

BIOPROMO

Bioprocess, Biomolecules

New continuous electrophoresis tools for innovative process of biomolecules purification

By Eléonore Adrey, 1st year

Supervisors: Isabelle Chevalot, Edith Lecomte-Norrant, Bruno Ebel, Xavier Framboisier

Keywords Electrophoresis Purification Biopharmaceuticals products Continuous bioprocess

BIOPROMO, IPSOMEL INNOVATION

General context, scientific issue

Today, most purification operations dedicated to biomolecules for therapeutic applications are carried out using chromatography. These techniques are very expensive, time consuming and have a major impact on the cost of producing biomolecules. [1] To reduce production costs, new technologies are being studied based on the properties of the biomolecules of interest and the impurities to be eliminated, such as free flow electrophoresis.

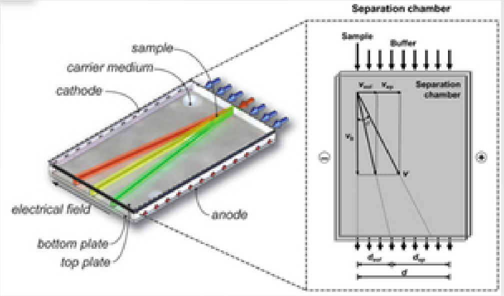
Objectives and stakes

The aim of this project is to demonstrate the benefits of using free flow electrophoresis compared with chromatography techniques for the purification of biomolecules for pharmaceutical use. The work is based on two aspects. The first is the development of electrophoresis technology to obtain an optimized chip that meets the various technical characteristics (laminar flow, electric field, adaptation of materials), while at the same time scaling up in terms of thickness in order to achieve a continuous flow rate that will enable industrial volumes to be treated. The second phase of the project is based on understanding the separation phenomena involved.

After establishing proof of concept on commercial molecules (peptides, proteins, antibodies), the aim is to integrate the technology developed into a complete bioprocess that can be scaled up to pilot and industrial scale.

Methodology / Experimental approach

- The first step of the project is to develop the electrophoretic purification system to understand the physical phenomena and resolve the problems such as voltage loss or hydrodynamic disruptions. The chip is hand-made, and an experimental design approach is used to characterize it in order to define the influence of the operating parameters on its functioning.
- Secondly, the tool will be tested on a panel of biomolecules selected for their use in active pharmaceutical ingredients and produced from cell culture in order to define the operating conditions. Two examples are considered to prove the efficiency of the tool: the separation of molecules with similar physico-chemical characteristics from a synthetic mixture and the purification of a molecule of interest in a biological medium produced from cell culture.
- Finally, the results obtained by free flow electrophoresis will be compared with the results obtained by conventional chromatographic techniques to justify the use of this technique in a future industrial bioprocess.



Principle of molecule separation by free-flow electrophoresis [2]

Main results

Bibliographic research has shown that many parameters require to be controlled and tested by experiments in various conditions. However, knowledge of free-flow electrophoresis has not yet allowed the emergence of an industrial tool that operates continuously and is able to compete with chromatography. In particular, issues with bubbles in the separation chamber appear after several hours of use, or the materials used are not conducive to cooling the system.

Preliminary results showed using DOE with 15 experiments that the design of the electrophoretic system and the operating conditions (buffer's pH, electric field, samples concentration, separation chamber size, flow rate, viscosity, conductivity) have a significant influence on the separation of commercial molecules such as fluorescein, rhodamine B, rhodamine 6G with different electrophoretic mobilities even with close sizes.

The migration of molecules of interest and their purification depends on both the operating conditions and the design of the electrophoretic system. These results suggest that purification conditions need to be optimized for each bioprocess by optimizing both design of the chip and operating conditions.

References

[1] Labrou, N. E. Protein Purification: An Overview. In Protein Downstream Processing: Design, Development and Application of High and Low-Resolution Methods; Labrou, N. E., Ed.; Methods in Molecular Biology; Humana Press: Totowa, NJ, 2014; pp 3–10. https://doi.org/10.1007/978-1-62703-977-2_1.

[2] Lee, Y.; Kwon, J.-S. Microfluidic Free-Flow Electrophoresis: A Promising Tool for Protein Purification and Analysis in Proteomics. Journal of Industrial and Engineering Chemistry 2022, 109, 79–99. https://doi.org/10.1016/j.jiec.2022.02.028

Tuning the bioproduction, in bioreactors and controlled microenvironments, of Wharton’s jelly-derived human mesenchymal stromal cell secretomes

By Kévin Audoux, 1st year

Supervisors: Eric Olmos, Jessica Schiavi-Tritz

Keywords Bioprocesses Mesenchymal stromal cells Microenvironment Secretome bioproduction

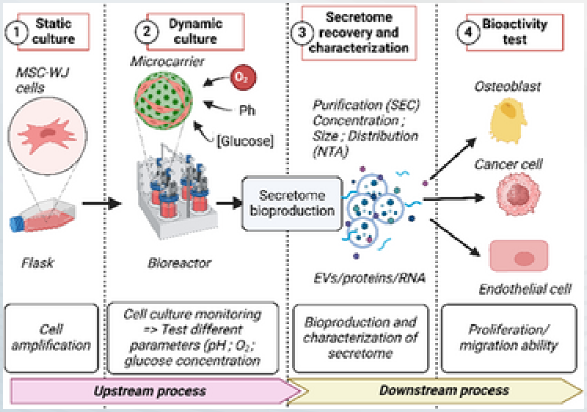
BIOPROMO

General context, scientific issue

Human Mesenchymal Stromal Cells from Wharton’s Jelly (WJ-MSCs) produce a promising secretome for regenerative medicine. However, the scaling-up of the production while maintaining the quality is crucial for a therapeutical application [1]. Controlled bioreactors offer, a priori, an efficient and reproducible approach to increase the production.

Methodology / Experimental approach

WJ-MSCs were cultivated in Ambr®250 modular bioreactor vessel with Synthemax II microcarriers with various oxygen concentrations (2, 10 and 19 % of oxygen saturation) to assess the impact of the concentrations on cell growth and secretome production. A culture monitoring was conducted to analyse the growth kinetics of the cells and their metabolism (glucose, lactate, glutamine) throughout the culture period. After achieving the highest cell densities under each condition, cells were incubated for 48 hours in serum-free medium where the secretome of cells is released and is called conditioned media (CM). This approach aimed at removing exogenous EVs and proteins contained in the serum, to hold only those produced by cells. Subsequently, EVs and proteins were purified in different fractions with a Size Exclusion Chromatography (SEC), followed by their characterisation by using Nanoparticle Tracking Analysis (NTA) and Bradford protein assay (BCA), respectively. Finally, secretome quality and functionality were evaluated through bioactivity assays to calculate their proliferation and migration capacity, using the scratch test method on osteoblasts.



Experimental approach for secretome production from WJ-MSCs using a controlled bioreactor

Objectives and stakes

This study aims to develop a robust production bioprocess of the secretome from WJ-MSCs that enables both high-volume secretion and the preservation of bioactive properties. Furthermore, altering the cellular environment (oxygen, pH, nutriment availability) impacts cell growth and the secretome composition [2,3]. The understanding and optimization of these factors hold the key to unlock the full therapeutic potential of these components. The utilization of bioreactors, that enable a better control of culture parameters, introduces additional stakes, allowing for precise modulation of secretome production.

Main results

In the experimental conditions with 2 and 10 % oxygen concentration, a twofold increase in cell concentration was observed compared to the 19 % condition. Moreover, the specific glucose metabolic consumption rate was significantly 2 to 3 times higher at 2 and 10 of oxygen saturation, than in the culture controlled at a concentration of oxygen of 19 %. Surprisingly, despite the higher cell concentrations, the concentration of particles and proteins remained equivalent across all conditions. Furthermore, bioactivity assays demonstrated that both EVs and the concentrated secretome were able to enhance the proliferation and migration of osteoblasts in a dose-dependent manner. Notably, EVs and secretome derived from MSCs cultured with 2 % of oxygen exhibited the most pronounced effects. To conclude, these findings suggest that the 2 % oxygen condition, does not directly quantitatively increase the production of WJ-MSC secretome, but may enhance its quality and bioactivity, especially for tissue regeneration. Further research could clarify these mechanisms, potentially leading to specifically optimize the culture conditions for regenerative medicine applications.

References

[1] J. Y. Kim et al., « Bolstering the secretion and bioactivities of umbilical cord MSC-derived extracellular vesicles with 3D culture and priming in chemically defined media », Nano Convergence, vol. 9, no 1, p. 57, déc. 2022, doi: 10.1186/s40580-022-00349-z.

[2] S. Chen, F. Sun, H. Qian, W. Xu, et J. Jiang, « Preconditioning and Engineering Strategies for Improving the Efficacy of Mesenchymal Stem Cell-Derived Exosomes in Cell-Free Therapy », Stem Cells Int, vol. 2022, p. 1779346, mai 2022, doi: 10.1155/2022/1779346.

[3] C. Almeria, R. Weiss, M. Keck, V. Weber, C. Kasper, et D. Egger, « Dynamic cultivation of human mesenchymal stem/stromal cells for the production of extracellular vesicles in a 3D bioreactor system », Biotechnol Lett, févr. 2024, doi: 10.1007/s10529-024-03465-4.

Multiscale modeling of a monoclonal antibody production bioprocess for its optimal control

By Alejandro Avilan Garzon , 3rd year

Supervisors: Eric Olmos, Bruno Ebel, David Pfister

Keywords Modelling Bioprocess Antibody Chinese Hamster Ovary cells CHO

BIOPROMO, YPSO-FACTO

General context, scientific issue

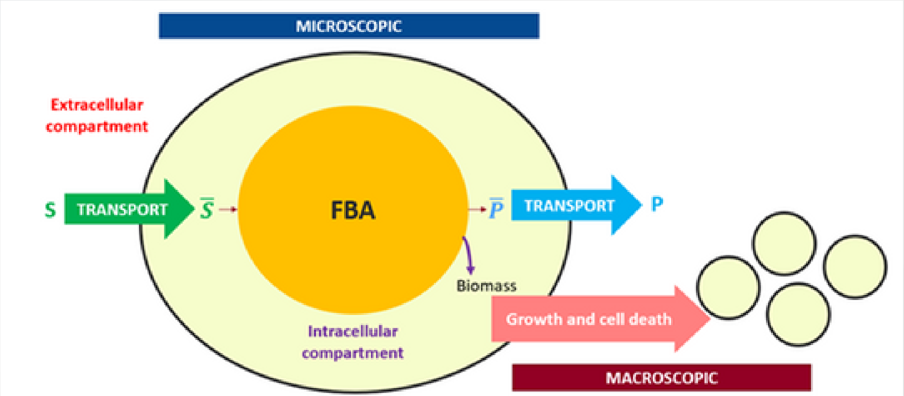
Monoclonal antibodies (mAbs) represent nearly 50% of the therapeutic protein market and are mostly produced via the CHO cell line [1]. Efforts to improve performance, robustness, and controllability to automate these production processes include the development of digital twins to simulate, test, and predict the system behavior quickly and at low cost [2]. However, this objective requires models, ranging from the microscopic (intra-cellular 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.

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 approach

- Experimental data: Collection of experimental kinetic data of CHO cell cultures in batch and fed-batch cultures carried out in Erlenmeyer flasks through measurements 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.



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 flask (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. It was also found that there is a 2-day delay between intracellular and extracellular IgG concentrations.
- With the aim of create a kinetic model that respects the atomic and mass balances, 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.

Multiscale modelling of bioleaching processes for the recycling of printed circuit boards waste

By Marc-Antoine Besch, 1st year

Supervisors: Eric Olmos, Agathe Hubau,
Céline Loubière

Keywords Bioprocess | Bioleaching | Modelling | Computational Fluid Dynamics (CFD) | Multiphase fluid flow | Printed Circuit Board | Bioreactor | Lattice-Boltzmann

BIOPROMO, BRGM

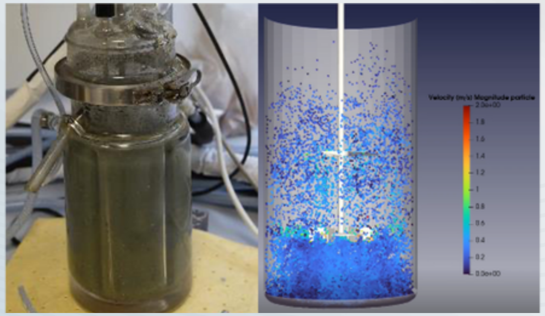
General context, scientific issue

Printed Circuit Board (PCB) wastes from electronic appliances represent an interesting source of metals such as copper that are now considered critical. Indeed, a growing demand of strategic metals required for the "green and sustainable" transition of the industry and economy impose the development and optimization of extractive operations. Bioleaching i.e., extractive metallurgy aided by microorganisms, is a promising recycling process [1].

Methodology / Experimental approach

Characterization of a bioleaching process in a stirred tank shall be conducted considering a 2-liter bioreactor which is currently operated by the BRGM (Orléans). Experimental studies will be focused on single-phase and then gas-liquid and liquid-solid (grinded PCB particles or gas) characterization. Determination of flow field, power input, minimal agitation rate for suspension (NjS) and the volumetrics oxygen transfer coefficient kLa will be determined while assessing the impact of the heterogeneous grinded PCB on those parameters.

Simulations are conducted using a lattice-Boltzmann approach [3]. First, CFD models for turbulence such as LES are evaluated using M-Star commercial software, then multiphase simulations for particles suspension and oxygen dissolution will be carried-out and confronted to experimental results in order to compare NjS, particle homogenization time and kLa. Finally kinetic reactions and bacterial bioleaching activity will be implemented in the CFD studies to first adjust the simulation models and then in-silico assess the effect of different parameters (particle size and properties, agitation rate, equipment geometry) in a general objective of optimization and scale-up.



Experimental bioleaching process for PCB recycling and computational simulations (CFD, particle velocity)

Objectives and stakes

Bioleaching occurs in a multiphase bioreactor. Grinded PCB (solid) are mechanically suspended in a culture medium (liquid) where bacteria such as Leptospirillum ferriphilum (solid) proceed to metal leaching in an aerated environment ensured with gas bubbles. The study of such dynamic and heterogeneous [2] (various granulometry of PCB waste) system can be aided by Computational Fluid Dynamics (CFD) methods that allow in-silico simulations of these operations. Such modelling may indeed give access to difficult to measure parameters (energy dissipation for instance) or help optimize the bioprocess.

Main results

CFD model for turbulence modelling (LES) has been chosen considering simulation accuracy versus computation time and capacity, allowing then to obtain main liquid-flow characteristics (Power number, Taylor scale) values. Determination of models for particle suspension is in progress, in order to correctly consider the heterogeneity in size, shapes and density of grinded PCB and identify a potential impact on the fluid flow and mixing.

Particles suspension and gas aeration experiments will help in choosing the right simulation models and parameters. Then the adjusted CFD model will be coupled with bioleaching kinetic reactions to assess the effect of PCB heterogeneities on the process and help in improving the bioleaching operation regarding specific metals for instance.

References

[1] A. Hubau, M. Minier, A. Chagnes, C. Joulian, C. Silvente, et A.-G. Guezennec, « Recovery of metals in a double-stage continuous bioreactor for acidic bioleaching of printed circuit boards (PCBs) », Separation and Purification Technology, vol. 238, p. 116481, mai 2020, doi: 10.1016/j.seppur.2019.116481.

[2] A. Barthet, H. Chauris, T. Romary, V. Semetey, et E. Chautru, « Advanced Granulometric Characterization of Shredded Waste Printed Circuit Boards for Sampling ». Rochester, NY, 22 novembre 2023. doi: 10.2139/ssrn.4640767.

[3] J. J. Derksen, « The Lattice-Boltzmann Method for Multiphase Fluid Flow Simulations and Euler-Lagrange Large-Eddy Simulations », in Multiphase Reacting Flows: Modelling and Simulation, vol. 492, D. L. Marchisio et R. O. Fox, Éd., in CISM International Centre for Mechanical Sciences, vol. 492. , Vienna: Springer Vienna, 2007, p. 181-228. doi: 10.1007/978-3-211-72464-4_5.

Enrichment of epigenomic and metabolic investigations in the bioprocess engineering of secretome

By Léa Blanchard, 1st year

Supervisors: Emmanuel Guedon, Natalia de Isla, Guillermo Barreto, Jessica Schiavi-Tritz

Keywords Mesenchymal stem cells Secretome Bioproduction Exposome

BIOPROMO, IMOPA , CECITA

General context, scientific issue

Secretome produced by Mesenchymal Stromal Cells (MSCs), uses like free-cell therapy, have a strong therapeutical potential1. However, it is not fully understood how the microenvironment affects phenotype, characteristics and secretome production by MSCs2.

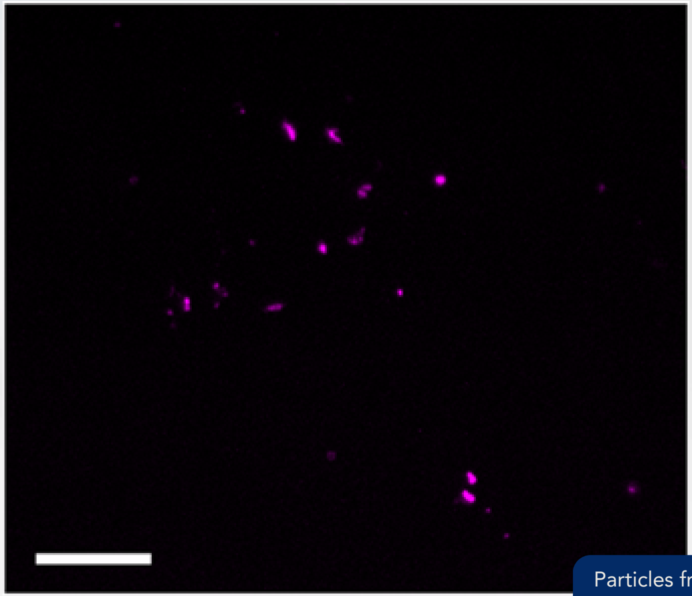
Objectives and stakes

This PhD project explores the impact of the microenvironment around cells on their production of secretome. The objectives are to (i) optimize MSC culture conditions to improve the bioproduction yield of secretome, and (ii) to evaluate their efficiency and therapeutic potential. By characterizing secretome produced by MSCs under optimized conditions, this research contributes to increase knowledges on secretome-MSC biology and secretome-based therapies.

Methodology / Experimental approach

WJ-MSCs are cultured in classical conditions (2D, static). During cell culture, two parameters are modified: mechanical stimulation and pH. At the end of the culture, the production of the secretome is compared across the four conditions. The secretome is characterised by its protein content using the BCA reagent (bicinchoninic acid, a colorimetric test), its size via Nanoparticle Tracking Analysis (NTA), and its bioactivity (migration test with osteoblastic cells). The composition of the secretome is studied by Western-Blot and microscopy.

The impact of the conditions on cell growth is evaluated by an automated system that measures both cell viability and cell count. Metabolites are monitored by a multiparametric analyser, the Gallery.



Particles from the secretome stained by immunofluorescence. Scale bar: 20 µm.

Main results

The results show that physiological or pathological pH, with or without mechanical stimulation, does not have a negative impact on cell growth or cell doubling time, supporting the application of these conditions in cell culture. Mechanical stimulation has a positive effect on particle production per cell, but does not significantly influence protein production or particle size, although particles are smallest under mechanical stimulation at a pathological pH. The secretome observed under the microscope confirms the presence of particles and the efficacy of the protocol.

References

1. Discher, D.E., Mooney, D.J., and Zandstra, P.W. (2009). Growth factors, matrices, and forces combine and control stem cells. Science 324, 1673–1677. https://doi.org/10.1126/science.1171643.
2. Phelps, J., Sanati-Nezhad, A., Ungrin, M., Duncan, N.A., and Sen, A. (2018). Bioprocessing of Mesenchymal Stem Cells and Their Derivatives: Toward Cell-Free Therapeutics. Stem Cells Int 2018, 9415367. https://doi.org/10.1155/2018/9415367.

Development of nanoparticles for anti-bacterial applications

By Laure Brice, 1st year

Supervisors: Ariane Boudier

Keywords Antibacterial properties | Metallic nanoparticles | Synthesis | KISS principle

BIOPROMO

General context, scientific issue

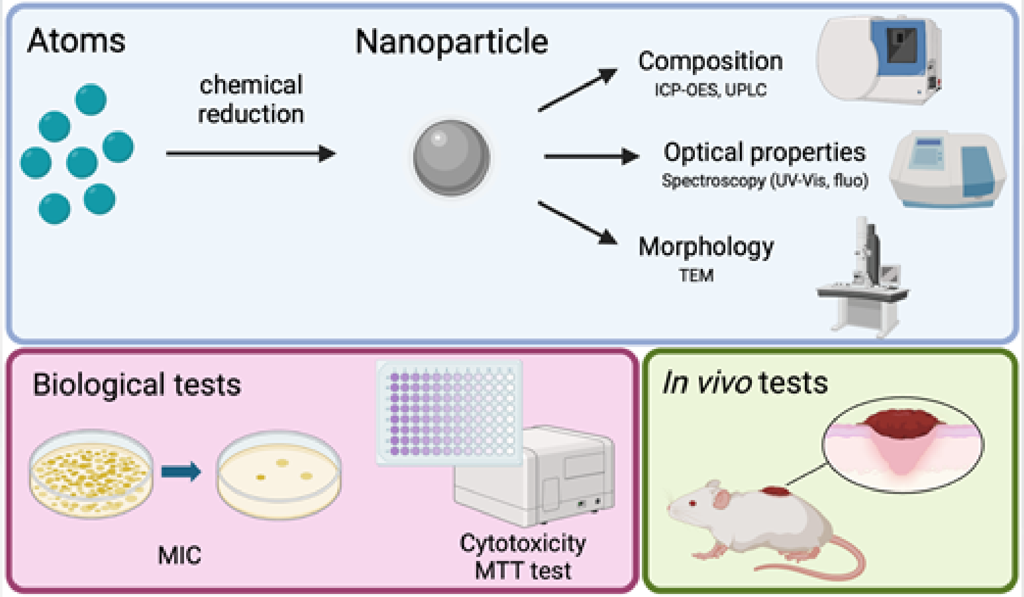
Antimicrobial resistance (AMR) is a major global health threat, jeopardizing the advances of modern medicine, making infections harder to treat, and increasing the risks associated with medical procedures such as surgeries and chemotherapy (1).

Objectives and stakes

Metal nanoparticles, with a size between 1 and 100 nm, can inhibit the growth of Gram-positive or negative bacteria or fungi and can destroy microorganisms (2). Each year, a significant number of research studies on metal nanoparticles for biomedical applications lead to clinical trials (3). Considering the increasing need for new antibacterial solutions, this thesis project aims to develop novel nanoparticles with antibacterial properties.

Methodology / Experimental approach

Synthesis of metallic nanoparticles can be done through chemical reduction, which requires the use of a reducing agent to donate electrons to metal ions (4). Thereby converting them into neutral metal atoms which aggregate to form nanoparticle nuclei. Chemical reduction is a versatile and widely used method for the synthesis of metal nanoparticles due to its simplicity (KISS principle, « Keep It Stupid Simple »), relatively low cost, and ability to produce nanoparticles of different sizes and shapes with good reproducibility. The size, shape, and distribution of the nanoparticles can be controlled by adjusting the reaction conditions, such as reactant concentrations, pH, temperature, and reaction time. The main objective is to control these parameters to achieve specific desired properties. Accordingly, tests for inhibiting bacteria and microorganisms are conducted to select nanoparticles that exhibit the most favorable properties. Subsequently, cytotoxicity tests on cells are performed to confirm the potential use of the selected nanoparticles without inducing toxicity. Finally, in vivo tests may be conducted with candidate nanoparticles to establish their potential for clinical use.



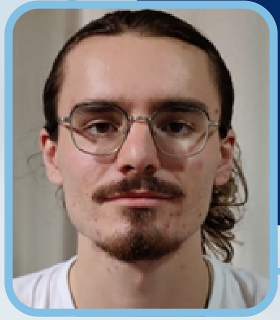
Experimental plan of the conception, characterization and use of nanoparticles.

Main results

Data and results are confidential.

References

1. Antimicrobial resistance [Internet]. [cité 30 avr 2024]. Disponible sur: https://www.who.int/news-room/fact-sheets/detail/antimicrobial-resistance
2. Salah I, Parkin IP, Allan E. Copper as an antimicrobial agent: recent advances. RSC Adv. 19 mai 2021;11(30):18179-86.
3. Home | ClinicalTrials.gov [Internet]. [cité 30 avr 2024]. Disponible sur: https://clinicaltrials.gov/
4. Jamkhande PG, Ghule NW, Bamer AH, Kalaskar MG. Metal nanoparticles synthesis: An overview on methods of preparation, advantages and disadvantages, and applications. Journal of Drug Delivery Science and Technology. 1 oct 2019;53:101174.



Optimization of production of Mesenchymal Stem Cells (MSC) in stirred tank bioreactors for therapeutic purpose

By Gauthier Burgess, Study engineer

Supervisors: Isabelle Chevalot, Celine Loubière, Jessica Schiavi-Tritz

Keywords Mesenchymal stem cells | Bioproduction | Process | Scale-up | Optimization

BIOPROMO, CELLEASY

General context, scientific issue

Innovative cellular therapies using mesenchymal stem cells (MSC) are gaining in interest and becoming a major issue for cellular research and medical applications in a wide range of pathologies. A major problem is their availability in sufficient quantities. MSCs are difficult to obtain in large quantities, and complex to grow in flasks without incurring excessive production costs.

Objectives and stakes

The OPTI-STEM2 project, in which the LRGP is a partner, aims to define and optimize a means of producing MSCs in bioreactors. The ultimate aim is to democratize and facilitate their access to research and therapeutic applications. This will significantly reduce the production costs usually associated with MSCs expansion [1]. This is achieved by cultivation on small beads (from 125 µm to 300 µm) called microcarriers (µP) in stirred instrumented bioreactors. It is therefore important to be able to set up a scale-up process to produce larger cell quantities while stabilizing MSCs quality in line with current Good Manufacturing Practices (GMP).

Several researchers are working to optimize various parameters such as agitation speed, medium definition and µP selection. The latter, being the site of MSCs attachment and proliferation, is the critical parameter to be defined in the first instance.

Methodology / Experimental approach

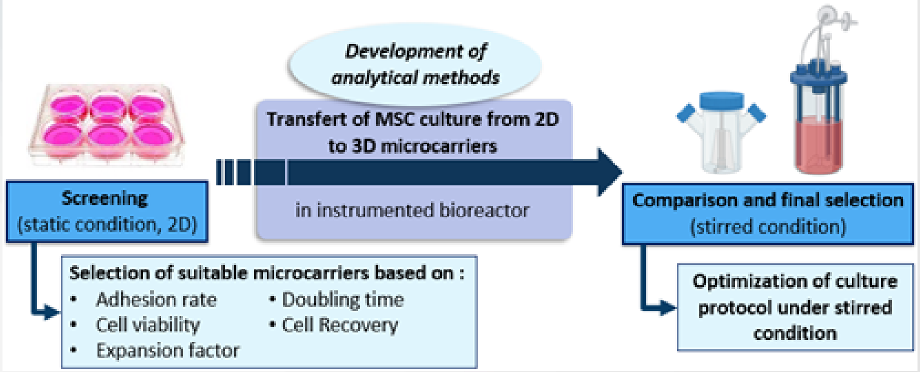
These experiments are carried out using a Design of Experiment (DoE) approach to ensure parameter optimization, reproducibility and quality of the MSCs produced in compliance with GMP.

The DoE is defined with initial MSC and µP concentrations and type as input and adhesion rate, doubling time, expansion factor and viability at the end of kinetics as output. This is in addition to the associated costs and cell recovery processes specific to each µP.

Adipose MSCs are grown in flasks before being inoculated for 7 days in spinner cultures with µP. Selection is carried out via culture in spinner, then validated on a 1L scale in an instrumented stirred bioreactor.

Additions of µP are made during culture when a threshold of cell per µP is exceeded [2]. This allows cells to migrate bead-to-bead to continue growing on new surfaces. The limits of µP and MSC concentrations can thus be determined.

Results are retrieved offline by daily sampling. MSC on µP thus recovered have their nuclei stained with DAPI/methanol. A fluorescence microscope (UV light) is then used to observe MSC adhesion and proliferation. Quantitative results are obtained by image processing using the routine software defined by Loubière C. [3]. Physiological monitoring is carried out by daily measurement of substrates and biproducts concentration in the medium by photometric analysis.



Development of analytical methods

Transfert of MSC culture from 2D to 3D microcarriers

in instrumented bioreactor

Screening
(static condition, 2D)

Selection of suitable microcarriers based on :
- Adhesion rate
- Cell viability
- Expansion factor
- Doubling time
- Cell Recovery

Comparison and final selection
(stirred condition)

Optimization of culture protocol under stirred condition

Transition from 2D culture to 3D culture

Main results

Four commercial microcarriers, called here µP-A, µP-B, µP-C and µP-D to respect the project confidentiality, were selected upstream, validating static flask adhesion tests. They were then tested in 120 mL spinner. µP-A and µP-B were discarded for reasons of significant lower cell proliferation and viability. µP-C was confirmed as viable for scale-up testing in a bioreactor. µP-D will be tested soon, being promising for simplified cell recovery.

The bead-to-bead additions enabled us to determine the critical final concentrations of µP and MSCs not to be exceeded. Above these levels, cell concentration and viability decline.

The most promising µP will be then selected to adapt and validate the protocol for a 1L scale-up. To do so, performances regarding the cell detachment and recovery process will be addressed and potentially optimized. The residual µP that may be present in the final solution is a major problem for analytical quality control instrumentation and GMP compliance. This last point will therefore be a key issue for the future.

References

[1] Jankovic M.G. et al., Stem Cells Transl. Med. 2023. 71 :103393
[2] Chen S. et al., Stem Cells Transl. Med. 2021, 10:1329-42
[3] Loubière C., HAL-UL. 2018. 99

Screening, separation and identification of metal-chelating peptides in protein hydrolysates

By Jairo Andrés Camaño Echavarría, 3rd year)

Supervisors: Laetitia Canabady-Rochelle, Katalin Selmeczi

Keywords Protein Hydrolysis Screening Metal-chelating peptides By-products Tilapia scale Sunflower meal

BIOPROMO, L2CM

General context, scientific issue

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 [1] e.g., antioxidant, antihypertensive, antimicrobial, and metal-chelating [2].

Objectives and stakes

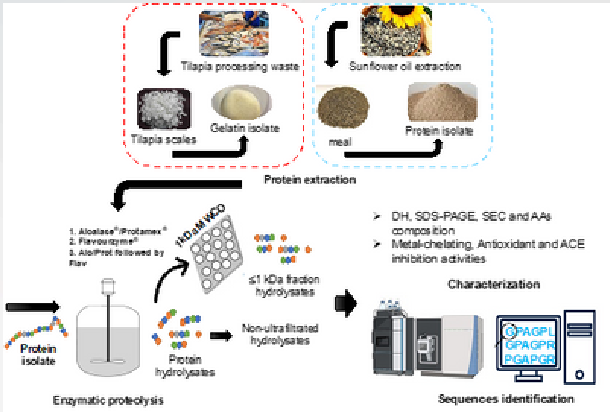
This PhD thesis aims to investigate the use of two agro-industrial by-products, i.e., red Tilapia scales and sunflower meal, for the preparation, characterization and identification of metal-chelating peptides by settingup screening and separation techniques based on UV-spectroscopy, surface plasmon resonance (SPR), switchSENSE®, and immobilised metal affinity chromatography (IMAC).

Methodology / Experimental approach

The Red Tilapia (Oreochromis spp.) scales and sunflower meal by-products were used to produce protein isolates (PI) by a hydrothermal extraction and an isoelectric point precipitation, respectively. Then, the PI were used to produce hydrolysates using industrial mixture of enzymes (i.e., Alcalase®, Alc; Flavourzyme®, Flav, and Protamex®, Prot), either used alone or sequentially (i.e., Alcalase® followed by Flavourzyme® or Protamex® followed by Flavourzyme®). The hydrolysates, whole and ultrafiltrated onto 1 kDa membrane, were physico-chemically characterized (degree of hydrolysis (DH), peptide concentration, molecular weight distribution and amino acids (AA) composition). Besides, their biofunctional activity (Ni2+, Cu2+, Fe2+-metal-chelating ability) and their bioactivity (radical scavenging, reducing power, antimicrobial and antihypertensive activities) were also investigated. Finally, in order to understand the relationship between the biofunctional and the bioactivity of peptides present in hydrolysates, a LC-MS/MS analysis was carried out to identify the peptide 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



Experimental set up used to produce biofunctional and bioactive peptides from Tilapia scale and sunflower meal by-products

Main results

The protein content initially present in sunflower meal (46.10 %) and Tilapia scale (40 %) increases up to 90.90 and 95 % upon protein extraction, respectively. For Tilapia scale gelatin, although Alc+ Flav hydrolysate shows the highest DH, the highest biofunctional properties are found unexpectedly in Alc one, therefore sequential hydrolysis seems not to improve the investigated hydrolysate properties for this resource. For sunflower meal protein hydrolysates, Prot alone treatment exhibits the highest the Fe2+-chelating, inhibition of Cu2+-induced reactive oxygen species production and ABTS scavenging activity. Meanwhile, sequential hydrolysates enhance the inhibition of Fe3+-induced ROS production and the reducing power. LC-MS/MS analysis confirms the presence of peptide sequences with high content of Gly, Pro and Ala, which might offer potentially metal-chelating and antioxidant properties in gelatin hydrolysates, while, His, Glu, Asp and Arg are identified as potentiating AA residues for the metal-chelating and antioxidant properties of sunflower meal protein hydrolysates.

Development of a coupled thermo-mechanical and enzymatic process for the depolymerization of Nylon from tights

By Pilar Chavez Linares, 3rd year

Supervisors: Isabelle Chevalot, Sandrine Hoppe

Keywords Biocatalysts · Enzyme production · Extrusion · Nylon · Elastane · Textile recycling

BIOPROMO, GÉNIE DES PRODUITS, ECOLLANT SAS

General context, scientific issue

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.

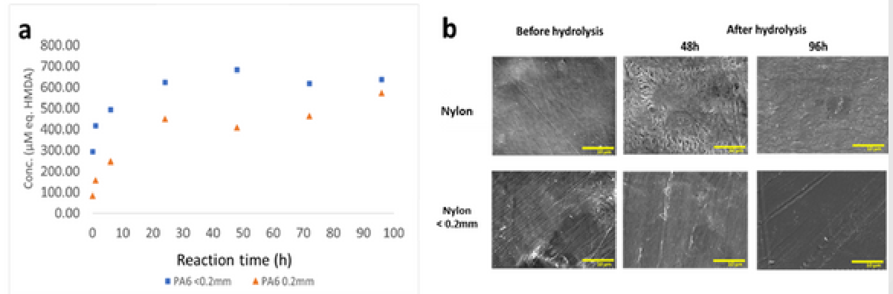
Objectives and stakes

The main objective of this project is the development of an environmentally friendly process for the hydrolysis of Nylon (polyamide, PA), which is one of the main polymeric components of tights. For this purpose, a thermomechanical process has been studied for the separation of Nylon and elastane in order to recover Nylon. This study is carried out on a laboratory scale. In addition, an enzymatic process using specific nylon hydrolases is applied for the hydrolysis of Nylon.

Methodology / Experimental approach

Three approaches are considered in this project. First, Nylon and elastane are blended together, making it difficult to separate the elastane. These fibers have different physicochemical properties; therefore, a heat treatment in the extrusion is envisaged to degrade the elastane without degrading the Nylon, followed by solvent dissolution to remove any remaining degraded elastane. A second approach is the modification of Nylon, which must have a reduced crystallinity index and a high specific surface area to facilitate enzymatic attack. Finally, Nylon specific enzymes are produced to identify the degraded products[1]–[3]. Different reaction conditions, such as temperature and pH range and enzyme loading, are studied. Afterwards, the coupling of thermomechanical and enzymatic treatments will be studied.

The hydrolysis reactions are monitored by derivatization of primary amino groups which are established by the o-phthalaldehyde assays (OPA) [4] and the residual material will be characterized with scanning electron microscopy (SEM). Also, 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 of the polymer [5]



Performance of specific enzymes (ENZ) for Nylon a) Derivatization of primary amines molecules released, b) SEM images of the Nylon 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.
Specific enzymes have demonstrated the ability to hydrolyze amide functions. However, these enzymes need to be modified genetically in order to increase their thermostability and their specificity towards Nylon. So far, nylon hydrolases have been shown to degrade nylon with a slow reaction rate. This degradation can be observed by scanning electron microscopy (SEM) as it is shown in the illustration (b); the surface of Nylon films is rough after 48h. This is due to the high crystallinity and its high Tg (around 56°C). It is important to consider the pre-treatment of the material, thus, it is currently being studied how to modify properties such as the decrease of crystallinity index by amorphization, as well as the increase of specific surface area of the material in order to increase the hydrolysis rate of the enzymatic attack which has been demonstrated using fine powder or using nylon foams.

References

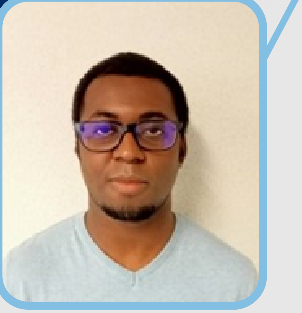
[1] S. Negoro et al., J. Biol. Chem.,2012, 5079–5090.
[2] C. Silva et al., Biocatal. Biotransformation, 2004, 357–360
[3] H.Puetz et al., ACS Sustainable Chemistry and Engineering, 2023 .
[4] A. Eberl et al., J. Biotechnol., 2009, 207–212
[5] F. Di Bisceglie. et al," Polymers", 2022 411

Development of an innovative bioleaching process for the treatment of limonitic nickel laterites – BIONICKEL.

By Samir Daniel, 3rd year

Supervisors: Eric Olmos, Anne-Gwénaëlle Guezennec

Keywords Bioprocess Nickel Cobalt Laterite Reductive bioleaching



BIOPROMO, BRGM

General context, scientific issue

Limonitic nickel laterite are oxidized ores mainly composed of goethite (FeOOH) which host up to 2 % of nickel and 0.5 % of cobalt [1]. Recently, the bacterial catalysis of goethite dissolution has been highlighted using iron reductive acidophilic microorganisms like Acidithiobacillus (At.) ferrooxidans in less energy-consuming conditions (30°C, atmospheric pressure) than traditional Pressure Acid Leaching processes (220 - 270 °C, 60 bars) [2].

Objectives and stakes

The objective of this work is to develop a continuous reductive bioleaching process at pilot scale to extract nickel and cobalt from laterites of New Caledonia. This study is divided into three steps, using shake flasks and bioreactors up to 4 L:

1.Determination of experimental conditions that favour bacterial growth.

2.Study of the biological ferric iron reduction mechanism with sulphur as substrate.

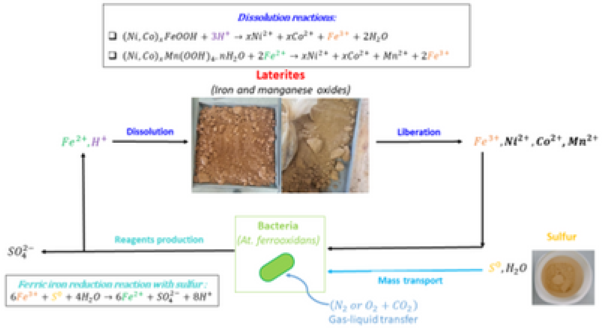
3.Optimization of operating parameters in a continuous bioreactor to promote iron bio-reduction performance, metals dissolution rates and reduce chemical reagents consumption.

Methodology / Experimental approach

*Bacterial growth: By Thoma cell counting method.

*Iron reduction kinetics: Redox monitoring using an Ag/AgCl redox probe and a correlation with the Fe(III)/Fe(II) ratio[3].

*Leaching kinetics: By MP-AES analysis of the pregnant leaching solution and mass balance with mineral composition.



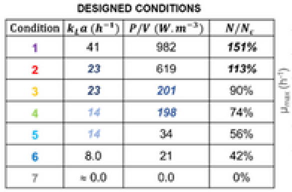
Reductive bioleaching of limonitic nickel laterites scheme.

Main results

In literature, few studies of kinetics using acidophilic bacteria in literature consider mass transfer and mass transport limitations, which cause non-optimal results [4]. In order to identify and lift those limitations: a methodology based on the use of the gas-liquid mass transfer coefficient , the power dissipation and the critical agitation rate to design shake flasks operating conditions was developed [5–7].

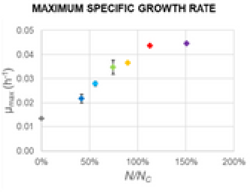
It was used to study the growth of At.ferrooxidans by oxidizing elemental sulphur at 30°C following this reaction:

$$2\,S^0 + 3\,O_2 + 2\,H_2O \rightarrow 2\,SO_4^{2-} + 4\,H^+$$



DESIGNED CONDITIONS

Condition	$k_La\ (h^{-1})$	$P/V\ (W.m^{-3})$	N/N_c
1	41	982	151%
2	23	619	113%
3	23	201	90%
4	14	198	74%
5	14	34	56%
6	8.0	21	42%
7	≈ 0.0	0.0	0%


MAXIMUM SPECIFIC GROWTH RATE

In literature, few studies of kinetics using acidophilic bacteria in literature consider mass transfer and mass transport limitations, which cause non-optimal results [4]. In order to identify and lift those limitations: a methodology based on the use of the gas-liquid mass transfer coefficient , the power dissipation and the critical agitation rate to design shake flasks operating conditions was developed [5–7]. It was used to study the growth of At.ferrooxidans by oxidizing elemental sulphur at 30°C following this reaction: .

References

[1] E. Fritsch, L. Bailly, B. Sevin, Atlas des latérites nickélifères de Nouvelle-Calédonie. Les gisements de nickel latéritique de Nouvelle-Calédonie, volume V 2017.

[2] C. A. du Plessis, W. Slabbert, K. B. Hallberg, D. B. Johnson, Hydrometallurgy. 2011, 109 (3–4), 221–229. DOI: https://doi.org/10.1016/j.hydromet.2011.07.005.

[3] G. Yue, A.-G. Guezennec, E. Asselin, Hydrometallurgy. 2016, 164, 334–342. DOI: https://doi.org/10.1016/j.hydromet.2016.06.027.

[4] B. Pokorna, M. Mandl, S. Borilova, P. Ceskova, R. Markova, O. Janiczek, Appl. Environ. Microbiol. 2007, 73 (11), 3752–3754. DOI: https://doi.org/10.1128/AEM.02549-06.

[5] J. M. Seletzky, U. Noak, J. Fricke, E. Welk, W. Eberhard, C. Knocke, J. Büchs, Biotechnol. Bioeng. 2007, 98 (4), 800–811. DOI: https://doi.org/10.1002/bit.21359.

[6] N. Mehmood, E. Olmos, J.-L. Goergen, F. Blanchard, P. Marchal, W. Klöckner, J. Büchs, S. Delaunay, Biochem. Eng. J. 2012, 68, 25–33. DOI: https://doi.org/10.1016/j.bej.2012.06.021.

[7] E. Olmos, K. Loubiere, C. Martin, G. Delaplace, A. Marc, Chem. Eng. Sci. 2015, 122, 545–554. DOI: https://doi.org/10.1016/j.ces.2014.08.063.

Valorization of ferulic acid from plant biorefinery by enzymatic synthesis for the production of bio-sourced and antioxidant building blocks and polymers

By Felipe Domingues Blanco, 2nd year

Supervisors: Yann Guiavarc'h, Catherine Virot-Humeau

Keywords Ferulic acid · Antioxidant · Biocatalysis · Polymer · Building block

BIOPROMO

General context, scientific issue

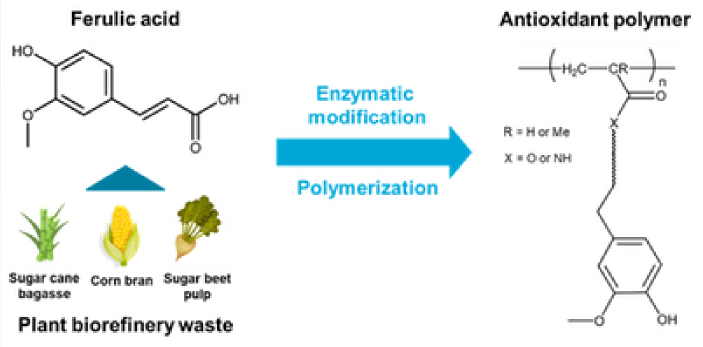
Ferulic acid is a phenolic acid present in plant biorefinery effluents, reaching concentrations as high as 8 g/kg in sugar beet pulp [1]. As potent antioxidant, this molecule is interesting to cosmetic and biomedical fields, where studies have shown its ability to be used as an anti-inflammatory and antitumoral agent. The acid presence in residual biorefinery effluents greatly destabilizes and alters 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 through different routes of enzymatic reactions. Further, the most promising route will be optimized and used for the study of polymerization and polymers properties.

Methodology / Experimental approach

Several enzymatic routes will be studied to modify the ferulic acid molecule aiming to functionalize it for further controlled radical polymerization, a type of polymerization with the ability to produce polymers with high molecular weight. The different pathways will be assessed to determine their feasibility through small-scale experiments, to verify if the desired products are formed during the reaction. After, 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 different parameters (temperature, molar ratio of substrates, enzyme load, duration) will be optimised. Next, 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, purification processes will be developed, both for the final monomer and intermediary products, to characterize their antioxidant properties. Finally, the production of the polymer will allow the test of its mechanical performance and antioxidant property.



Ferulic acid valorization route

Main results

Samples were analyzed with HPLC coupled with PDA and MS for detection and determination of the products formed. Novel enzyme acyl transferase from Mycobacterium smegmatis and the commercial lipase Lipozyme 435 were tested in the conversion of ferulic acid (FA) and its hydrogenated derivative, dihydroferulic acid (DHFA). The DHFA was more reactive and was selected as the starting substrate, as it can be easily obtained by chemical hydrogenation of FA with palladium catalyst. Comparing the enzymes, the lipase had better overall performances, resulting in up to 74% yield in the first step of the pathway, and experiments with this enzyme demonstrated the production of the desired monomer in small amounts. Finally, for the first step of the pathway, a scale up was performed using the immobilized enzyme and a rotating bed reactor. A purification method for this step was also developed, which allowed to confirm the intermediary product molecular structure through proton NMR.

References

[1] N. Kumar, V. Pruthi, Biotechnol Rep (Amst). 4, 86–93 (2014).
[2] A. Fiorentino et al., J. Agric. Food Chem. 51, 1005–1009 (2003).
[3] A. Khalil, C. Gerardin-Charbonnier, H. Chapuis, K. Ferji, J.-L. Six, ACS Sustainable Chem. Eng. 9, 11458–11468 (2021).

Metal chelating activity of protein hydrolysates from Californian red worm (Eisenia fetida) and fractions obtained by a crossflow ultrafiltration system

By Yhoan S. Gaviria Gaviria, 3rd year, Internship doctoral student

Supervisors: Laetitia Canabady-Rochelle, Edgar Zapata Montoya

Keywords Peptide Proteolysis Ultrafiltration Complexation Amino acids Affinity Bioactivity

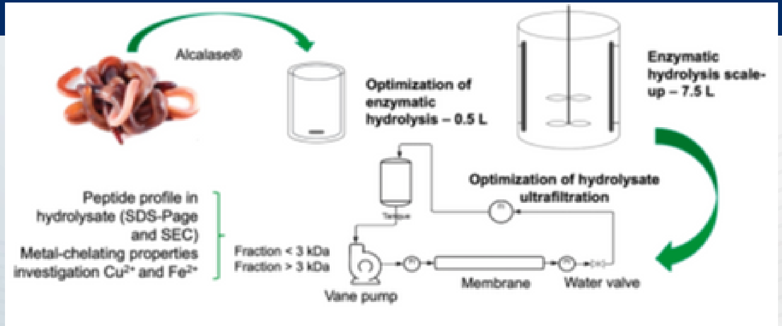
BIOPROMO, UNIVERSITY OF ANTIOQUIA (COLUMBIA)

General context, scientific issue

Regarding the ability to chelate minerals, the proteolysis process increases the availability of metal-binding sites by the peptide bond breakdown, which releases carboxylic groups, and the exposition of hidden binding sites in the protein structure [1]. The ability to probe metal-bound proteins and peptides is essential for understanding the biological role of metals. Non-essential metals also bind in the biological context—some lead to toxicity while some are therapeutic [2]. Metal ions, often at the core of structural stabilization, are essential for biological functionality including catalysis and inhibition or acceleration of aggregation [3]. Metal homeostasis is regulated by the metal-binding metallothioneins, that also protect against heavy metal toxicity [4].

Methodology / Experimental approach

Hydrolysis was carried out in a New Brunswick Bioflo & Celligen 310 bioreactor (Eppendorf, Germany) with a working volume of 6 L. The Californian Red Worms (Eisenia foetida) were added at a mass concentration of 20 g of protein per liter (g/L), and the pH was adjusted to 8.5 with 2N NaOH. Subsequently, the enzyme Alcalase 2.4 L® was added at an enzyme/substrate ratio (E/S) of 18% at 45°C, maintaining an agitation of 240 rpm. Then, the Californian red worm hydrolysate was ultrafiltrated and two fractions were obtained: higher than 3 kDa and less than 3 kDa. These fractions were freeze-dried and stored at -20°C for further analysis. The metal chelating capacity of metals such as iron, copper, and nickel was determined using various screening and separation approaches such as spectrophotometry, titration methodologies (Ion Selective Electrode, Isothermal Titration Calorimetry) and chromatography (IMAC-M2+). Additionally, peptide-metal interactions were determined using UV-Vis spectroscopy and circular dichroism. Peptides were identified using LC-MS/MS.



Synoptic scheme of experimental work under progress

Objectives and stakes

Therefore, the aim of this PhD doctoral mobility is to characterize the hydrolysate of the California red worm and its fractions obtained by tangential ultrafiltration, and to evaluate their chelating properties for iron, copper, and nickel, and demonstrate the complexes formation between peptide and metal.

Main results

Peptides from Californian red worms hydrolysates exhibit metal chelating properties, primarily those of smaller size (fraction less than 3 kDa). The smaller peptides show the highest chelating capacity for transition metals such as Cu2+, Fe2+, and Ni2+. The chelation capacity of these metals may facilitate the reduction of reactive oxygen species (ROS), producing an indirect antioxidant effect.

The peptide-metal complexes are formed by amino acids residues such as histidine, glutamic acid, and aspartic acid, which promote the affinity of the peptides with metal ions. These findings highlight the potential therapeutic applications of hydrolyzed peptides from Californian red worms in the treatment of diseases such as iron deficiency anemia and Menkes syndrome.

References

1. Ghosh, B.C.; Prasad, L.N.; Saha, N.P. Enzymatic Hydrolysis of Whey and Its Analysis. J Food Sci Technol 2017, 54, 1476–1483, doi:10.1007/s13197-017-2574-z.
2. Shalev, D.E. Studying Peptide-Metal Ion Complex Structures by Solution-State NMR. Int J Mol Sci 2022, 23.
3. Rao, S.R.; Schettler, S.L.; Horne, W.S. Metal-Binding Foldamers. Chempluschem 2021, 86, 137–145.
4. Krężel, A.; Maret, W. The Bioinorganic Chemistry of Mammalian Metallothioneins. Chem Rev 2021, 121, 14594–14648.

Combined experimental/numerical approach for the production and the characterization of new amino-acylases - Implementation in green N-acylation bioprocesses

By Laureline Gennesseaux, 4th year

Supervisors: Yann Guiavarc'h, Catherine Humeau

Keywords Enzymatic process | Aminoacylase | N-acylation | Enzyme structure-function relationships | Production of recombinant enzymes | Molecular modelling

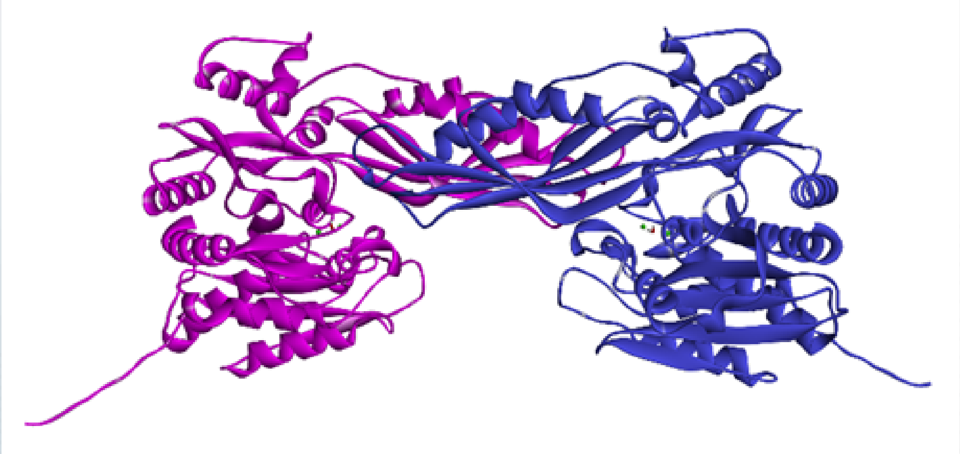
BIOPROMO

General context, scientific issue

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].

Methodology / Experimental approach

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.



3D structure of SamAA obtained by ColabFold after adding metal ions and catalytic water

Objectives and stakes

This project aims at developing a selective, efficient and ecofriendly 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 Escherichia coli system but allows to obtain at 45°C and pH8, in 48h, an apparent specific activity of 710 mg/L of N-α-lauroyl-L-lysine/100mg of proteins/L of concentrate crude extract with cobalt in the culture medium. A second heterologous expression test of SamAA with the S. lividans system is in progress to improve the results obtained to date. Heterologous expression work with E. coli was carried out with the Sam_ELA enzyme catalyzing N-acylation in the ε position of lysine, producing results similar to those obtained with SamAA. 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 almost finished 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.

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
[4] Jumper et al., Nature, 2021, 596:583-592

Sustainable production of bioactive surfactants from agro-resources by combinations of microbial and enzymatic processes in a zero-waste release concept.

By Dimitrios Giotis, 2nd year

Supervisors: Isabelle Chevalot, Lionel Muniglia

Keywords Bioprocesses Enzymes Biosurfactants Hempseed protein Single Cell Protein Protein Hydrolysates

General context, scientific issue

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, fibers, proteins, minerals, phytonutrients. Hemp proteins have gathered a huge interest for their various beneficial properties, so in order to acquire bioactive peptides and aminoacids from this plant, the extraction of proteins should be carried out and be followed by a subsequent hydrolysis of them.

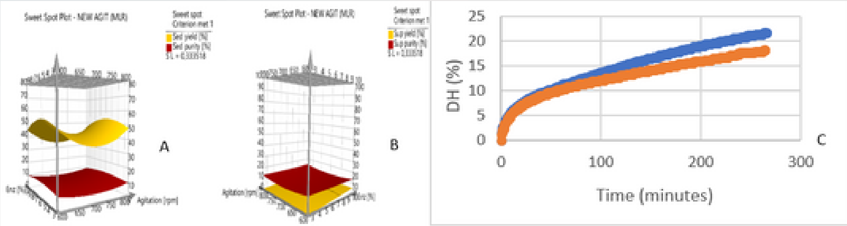
Microorganisms are able of producing high quantities of proteins2 and fatty acids. Consequently, it could be considered as essential to valorize a low (even negative) cost industrial by-product, glycerol, as the source in which microorganisms can grow in order to biosynthesize proteins and fatty acids.

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 / Experimental approach

Initially, the crushing of hempseeds was done by oil cold-pressing machine so hempseed meal was obtained (kindly donated by a local farm). The grinding of hempseed meal (for better yield in extraction step) has been done by a household blender and the protein extraction is envisaged to be catalyzed by enzymes (cell-wall degrading enzymes)4 in aqueous solution. In order to optimize the protein purity in the occurred products (sediment and supernatant) it was designed by MODDE an experimental design (DOE) of 18 trials with different enzyme concentrations (2.5%-10% v/w), agitation values (600-830 rpm) and hempseed:water ratios (0.33-0.5) which was carried out in spin-bioreactors for 4 hours at 50°C. The hemp proteins are hydrolyzed with different combinations of endo/exoproteases in aqueous media. The hydrolysis degree is being determined and the occured (oligo)peptides/aminoacids can subsequently be grafted with acyl groups so as to synthesize biosurfactants.



Schematic illustration of the optimization results for the sediment (A) and supernatant fraction (B) and a kinetics diagram of hydrolysis degree (DH-%) over time (minutes) for subtilisin (blue) and PR19 (orange) (C)

Main results

The results of DOE allow the determination of optimal conditions for hempseed protein extraction. After some cross-validation experiments which were carried out to check the validity of the model by MODDE it was found out that the optimal conditions regarding protein recovery for sediment and supernatant fraction individually were 6% v/w, 830 rpm, 0.398 and 7.5% v/w, 690 rpm, 0.40 which correspond to enzyme concentration, agitation value and hempseed:water ratio respectively. The protein purity was determined at 25.4% and 28.8% as well. The alkaline extraction-isoelectric precipitation (AE-IEP) as a reference method, was carried out in pH=10.0 and with the isoelectric point at pH=5.5 resulted in a protein content of 80% in the final product.

The hydrolysis of sediment after extraction with the subtilisin protease yielded a hydrolysis degree (DH) value of 21.5% while the hydrolysis of sediment with PR19® protease resulted in a DH value of 18.1%. Higher DH values are expected by using the supernatant fraction as the substrate for hydrolysis which is fully soluble in water. The characterization of the released peptides is in progress.

References

1. Sarubbo, L. A. et al. Biosurfactants: Production, properties, applications, trends, and general perspectives. Biochem. Eng. J. 181, 108377 (2022).
2. Ritala, A., Häkkinen, S. T., Toivari, M. & Wiebe, M. G. Single Cell Protein—State-of-the-Art, Industrial Landscape and Patents 2001–2016. Front. Microbiol. 8, 2009 (2017).
3. Bourkaib, M. C. et al. N-acylation of L-amino acids in aqueous media: Evaluation of the catalytic performances of Streptomyces ambofaciens aminoacylases. Enzyme Microb. Technol. 137, 109536 (2020).
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).

Optimization of polyphenol extraction from mature leaves of Xanthosoma mafaffa using deep eutectic solvents

By Essodjolon Kanabiya, 4th year, Doctoral trainee at LRGP for 10 months

Supervisors: Laetitia Canabady-Rochelle, Fabrice Mutelet, Mawuéna Novidzro

Keywords Xanthosoma mafaffa | Extraction processes | Polyphenols | Natural deep eutectic solvents | Green extraction | Antioxidant activity

BIOPROMO, CITHERE, UNIVERSITÉ DE LOMÉ (TOGO)

General context, scientific issue

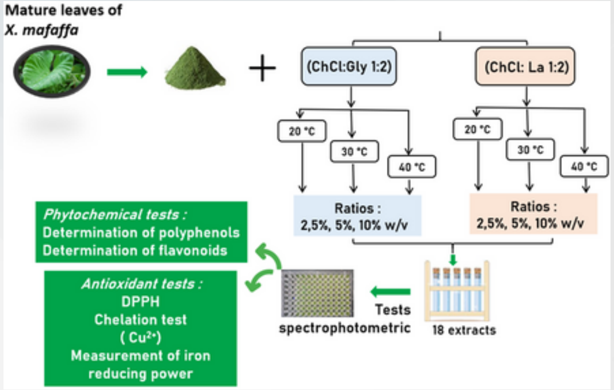
Natural substances, notably those of plant origin, have long been an important source of bioactive compounds. Among these, polyphenols, present in various plants, offer a wide range of health benefits thanks to their powerful antioxidant properties [1]. However, conventional extraction techniques consume large quantities of organic solvents, which are environmentally unfriendly and dangerous to human health, as well as being time consuming and energy intensive. Therefore, to overcome these drawbacks, the efficient extraction of phenolic compounds from medicinal plants requires an appropriate choice of extraction techniques, solvents and extraction parameters. Recently, green extraction has taken on major importance in research related to the production of biomolecules and polyphenols in particular [2]. Also, the food, cosmetics and pharmaceutical industries have made a transition from conventional extraction to green extraction processes, using alternative solvents that are cost-effective and environmentally friendly [3].

Objectives and stakes

This last part of this PhD aims to develop and optimize deep eutectic solvent (DES) extraction know as a potentially green and environmentally friendly extraction solvent to obtain higher yields of phenolic and flavonoid compounds from X. mafaffa mature leaves, and to evaluate their antioxidant activity.

Methodology / Experimental approach

Mature X. mafaffa leaves harvested in Togo were ground into a powder. Two natural deep eutectic solvents (NaDES) were selected for the extraction of phenolic compounds from X. mafaffa leaves: choline chloride-glycerol (ChCl-Gly) and choline chloride-lactic acid (ChCl-La) in a 1:2 (v/v) molar ratio. The powders were extracted by maceration at different solid/liquid ratios (2.5%, 5%, or 10% w/v) for 24 hours at three temperatures (20 °C, 30 °C, or 40 °C) in 20 mL of DES (ChCl-Gly or ChCl-La) using a thermostatic water bath. A total of 18 extracts were prepared. For each liquid extract, total phenolic compounds and flavonoids were quantified using the Folin-Ciocalteu and the aluminum trichloride assays, respectively. The antioxidant properties of each extract were then investigated. The antiradical activity of the extracts was determined by the DPPH● assay. In addition, the reducing power and metal chelating properties were studied by the reduction of the ferric complex ion K3Fe(CN)6 and the metal chelating test (Cu2+), respectively. Moreover, the effect of extraction temperature and solid/solvent ratio on the yield of secondary metabolites was statistically analysed by two-way analysis of variance (ANOVA).



Total phenolic content (TPC) in extracts of X. mafaffa leaves

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 Escherichia coli system but allows to obtain at 45°C and pH8, in 48h, an apparent specific activity of 710 mg/L of N-α-lauroyl-L-lysine/100mg of proteins/L of concentrate crude extract with cobalt in the culture medium. A second heterologous expression test of SamAA with the S. lividans system is in progress to improve the results obtained to date. Heterologous expression work with E. coli was carried out with the Sam_ELA enzyme catalyzing N-acylation in the ε position of lysine, producing results similar to those obtained with SamAA. 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 almost finished 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.

References

[1] Valko M, Leibfritz D, Moncol J, Cronin MTD, Mazur M, Telser J. Free radicals and antioxidants in normal physiological functions and human disease. Int J Biochem 2007;39(1):44-84.
[2] Pompeu DR, Silva EM, Rogez H. Optimisation of the solvent extraction of phenolic antioxidants from fruits of Euterpe oleracea using Response Surface Methodology. Bioresour Technol. 2009 Dec 1;100(23):6076–82.
[3] Alsaud N, Shahbaz K, Farid M. Application of deep eutectic solvents in the extraction of polyphenolic antioxidants from New Zealand Manuka leaves (Leptospermum Scoparium): Optimization and antioxidant activity. J Mol Liq. 2021 Sep 1;337:116385.

A lab-on-chip for rapid detection of bacteria

By Sephora Lahouari, 2nd year

Supervisors: Ariane Boudier, Jérémie Gouyon (LCPME)

Keywords Gold nanoparticles | Lectins | Dynamic complex | Fluorescence quenching | Atomic Force Microscopy | Molecular Dynamics

BIOPROMO

General context, scientific issue

We aim to design nanoprobes composed of gold nanoparticles (AuNP) functionalized by the lectin, Concanavalin A (ConA) for bacteria detection. These nanoprobes and interactions will be characterized and immobilized on microfluidic supports to propose a diagnostic tool in infectious diseases.

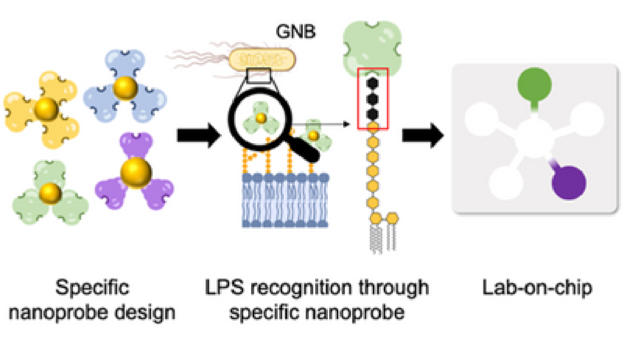
Methodology / Experimental approach

AuNP will be characterized according to a well-mastered protocol through a modified Turkevich's synthesis [2]. Their physicochemical properties (surface plasmonic resonance, hydrodynamic and core diameters, surface charge…) will be characterized before modification with the lectin.

Modification of AuNP with ConA will be undertaken via a direct route through a ligand exchange with the citrate ions composing the solvation layer of AuNP. Different methods will be used to decipher the binding mechanisms between AuNP and ConA, namely Fluorescence Quenching (FQ) and Atomic Force Microscopy (AFM) in force mode. The experimental results will be confronted to the theoretical behavior of the complex through Molecular Dynamics (MD) simulations.

We will next test their performance against LPS recognition and bacteria . It will be of crucial importance to determine the right conditions of pH, temperature and medium to allow for the best detection limit possible.

The last step of this project will be to immobilize different sugars on a paper lab-on-chip and allow the nanoprobe-bacteria complex to interact with them depending on the presence of a lectin (and hence, bacteria) specific to the sugars.



Development of a lab-on-chip for rapid detection of bacteria through nanoprobes

Objectives and stakes

The surface of gram-negative bacteria is composed of 75% of lipopolysaccharides (LPS). Their composition is specific of each strain and their identification allows for diagnosis [1]. Lectins are a class of proteins which possess specific carbohydrate-binding sites. Immobilizing lectins on top of AuNP allows for a wide range of detection methods to characterize the nanoparticle-lectin interactions as well as the nanoprobe-bacteria interactions.

Main results

AuNP were synthesized and characterized (3.3 ± 0.8 and 6.5 ± 0.4 nm for core and hydrodynamic diameters, respectively) with a surface charge of -30.2 ± 9.1 mV. Con A was directly added to AuNP to a final 1:1 molar ratio and were characterized. FQ, MD and AFM in Force Mode were used to decipher the nature of the interactions between AuNP and ConA.

AuNP-ConA showed a surface plasmon resonance peak value at 517 ± 1 nm versus 513 ± 1 nm for AuNP, confirming a change in their electronic environment. The thermodynamic parameters (ΔH, ΔS and ΔG) obtained with FQ, indicated a spontaneous binding between AuNP and ConA. FQ showed affinity constants (Ka) in the range of 108 and also indicated that the nature of the bonds were of low energy [3]. The low energy results were confirmed with AFM in Force mode which showed interaction forces of less than 150 pN. The predominance of a static mechanism was highlighted between AuNP and ConA up to room temperature meanwhile a dynamic mechanism predominates from 37° C to 60 °C. MD further confirmed the low energy interactions between AuNP and ConA.

References

[1] G. Klein et S. Raina, « Regulated Assembly of LPS, Its Structural Alterations and Cellular Response to LPS Defects », International Journal of Molecular Sciences, vol. 20, no 2, Art. no 2, janv. 2019, doi: 10.3390/ijms20020356.

[2] C. Boukoufi, A. Boudier, S. Lahouari, J. Vigneron, et I. Clarot, « Activity and reusability of immobilized gold nanoparticles for the catalysis of both oxidation and reduction reactions », Results in Chemistry, vol. 5, p. 100979, janv. 2023, doi: 10.1016/j.rechem.2023.100979.

[3] J. Beurton, P. Lavalle, A. Pallotta, T. Chaigneau, I. Clarot, et A. Boudier, « Design of surface ligands for blood compatible gold nanoparticles: Effect of charge and binding energy », International Journal of Pharmaceutics, vol. 580, p. 119244, avr. 2020, doi: 10.1016/j.ijpharm.2020.119244.

Chemical modification of folic acid: a promising strategy to improve stability while maintaining targeting in photodynamic therapy for cancer treatment

By Morgane Moinard, 3rd year

Supervisors: Céline Frochot, Nadira Delhem

Keywords Photodynamic therapy Photosensitizers Folic acid Ovarian cancer Peritoneal carcinomatosis

BIOPROMO, ONCOTHAI

General context, scientific issue

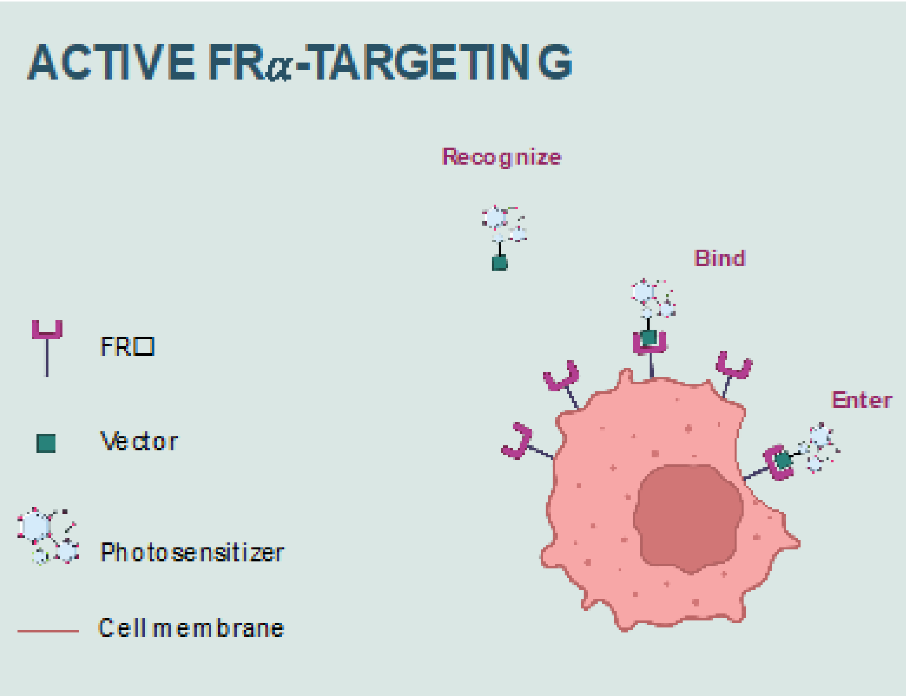
Folic acid (FA), or vitamin B9, is crucial for DNA and RNA synthesis, widely used in supplements and cancer treatment. However, FA is prone to degradation under adverse conditions1, compromising its biological activity and binding to folate receptors (FRα), which are overexpressed in cancers such as ovarian peritoneal metastases2,3.

Objectives and stakes

Our objective is to synthesize stable FA analogs targeting FRα, conjugated via a PEG spacer to a photosensitizer (PS) for PDT treatment of peritoneal carcinomatosis.

Methodology / Experimental approach

- Molecular docking to predict receptor affinity,
- Synthesis of FA analogues and coupling with PS,
- Photophysical properties analysis,
- In vitro and in vivo biological studies,
- Stability study using a Design of Experiment approach.



Principle of the active FRa-targeting.

Main results

The PSFAA, synthesized in 10 steps with a 19% yield, exhibited photophysical properties in ethanol similar to free Pyro-a (Φf = 0.39 and ΦΔ = 0.53 for free Pyro-a; Φf = 0.26 and ΦΔ = 0.41 for PSFAA). PSFAA showed no toxicity in OVCAR3 and SKOV3 ovarian cancer cells lines and demonstrated a dose-dependent response upon light exposure. Its PDT efficacy was confirmed by reduced IL-6 secretion in OC cell secretome. Preliminary stability tests revealed FAA's superior stability compared to FA.

References

[1] Gazzali M. et al., European Journal of Pharmaceutical Sciences, 2016, 93, 419–430.
[2] Parker N. et al., Analytical Biochemistry, 2005, 338, 284–293.
[3] Moinard M. et al., Pharmaceuticals, 2022.
[4] Moinard M. et al., Journal of Controlled released, 2024.

Purification of Nisin by ion exchange chromatography

By Amine Nekkaa, 1st year

Supervisors: Laetitia Canabady-Rochelle, Christelle Mathé, Laurence Muhr

Keywords Peptide Chromatography Separation Purification Optimization Antibacterial activity

BIOPROMO, PERSEVAL

General context, scientific issue

Nisin is a natural antimicrobial peptide produced by Lactococcus lactis strains. This first and only bacteriocin approved by the Food & Drug Administration is used as food additive and is a potential ingredient in pharmaceutical, veterinary and healthcare products. The major bottleneck for nisin to meet the growing market demand is the high overall production cost, related notably to its downstream process, which generally accounts for up to 80% of its production cost.

Methodology / Experimental approach

The NISINNOV project is constituted of 4 mains work-packages (WPs) led in various laboratories: (i) the nisin production and its in situ recovery (WP1), (ii) the nisin concentration and primary purification (WP2), (iii) the nisin purification by IEC chromatography (WP3; this LRGP PhD thesis recently begun) and (iv) the nisin scale-up implementation (WP4). In this PhD thesis, we plan to use expensive high-resolution separation techniques such as ion-exchange chromatography (IEC), since this is one of the most widely used high resolution techniques for nisin separation. The IEC process will be used at the final nisin purification process, starting on stream produced by other partners. This PhD thesis led at LRGP will be divided in 3 main tasks described hereafter.

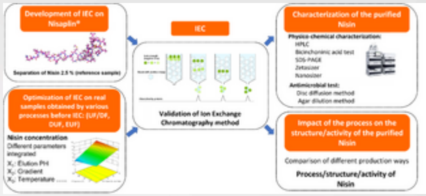
First, the cation-exchange chromatography will be developed on a commercial nisin sample (Nisaplin®) at 2.5% purity used as reference. The nisin purity and yield will be determined after IEC as a function of the experimental conditions tested. This chromatography will be carried out in frontal conditions and fractions will be collected for further analysis. The parameters investigated will be related to the column itself (i.e., nature of the chromatographic phase), the physico-chemical conditions, and the process parameters. After IEC, samples collected at the column outlet will be submitted to various analysis notably (i) to detect/identify and (ii) to quantify nisin peptide by antimicrobial and BCA tests.

Secondly, the IEC will be applied on the produced nisin fractions (Partner I, WP 2). The nisin samples produced will be submitted first to clarification followed by an ultrafiltration step constituted of either ultrafiltration/diafiltration (UF/DF), dynamic ultrafiltration (DUF) or electrofiltration (EUF). The three samples collected after this novel filtration strategy will be submitted to a IEC as developed in the first task of this PhD and compared to a commercial sample of nisin (Nisaplin®), submitted only to the cation exchange chromatography, as a reference sample. The three resulting nisin fractions will be analyzed, compared and quantified. The comparison of the various production routes will enable to determine the most appropriate one to obtain nisin with high purity.

Finally, the impact of the process will be investigated on the structure/activity of the nisin. Indeed, the effect of the purification process will be studied on the nisin peptide properties in terms of physico-chemical characteristics and antimicrobial activity in order to make structure/activity relationship.

Objectives and stakes

The Lactic acid bacteria (LAB), which produce nisin, require complex nutrients to grow. Thus, this increases both production costs, but also creates difficulties for further separation. This bottleneck clearly represents the limiting factor in the large-scale production of pure nisin. This PhD thesis aims to propose an efficient and scalable nisin downstream processing strategy (DSP), to produce nisin with different purity levels and with reduced costs, according to the target application. This DSP design will include notably ion exchange chromatography (IEC). The project results are expected to improve the current industrial nisin DSP practices and the development and implementation of more efficient/sustainable and cost-effective bio-manufacturing costs of all biotechnical products.



Overview of this research work.

Expected results

First, a review on separation processes applied to nisin and bacteriocin, commonly used to date will be written. Then, an IEC method will be developed on Nisaplin®, used as a reference. Then, this purification method will be optimized for improving nisin purification on real samples produced at lab partners, with different UF processes applied, and adapted to larger scale. This purification design will result in a nisin with high purification factor, recovery, and endowed with antimicrobial activity. Finally, the structure/activity relationship of nisin will be investigated as a function of the downstream processing.

References

[1] Hage, M., et al. (2021). Nisin-based coatings for the prevention of biofilm formation: Surface characterization and antimicrobial assessments. Surfaces and Interfaces, 27, 101564.

[2] Gharsallaoui, A., et al. (2016). Nisin as a food preservative: part 1: physicochemical properties, antimicrobial activity, and main uses. Critical Reviews in Food Science and Nutrition, 56(8), 1262 1274.

[3] Karam, L., et al. (2013). Nisin adsorption on hydrophilic and hydrophobic surfaces: evidence of its interactions and antibacterial activity. Journal of Peptide Science, 19(6), 377-385.

[4] Zhang, W., et al. (2018). Optimization of RDM-UF for alfalfa wastewater treatment using RSM. Environmental Science and Pollution Research, 25, 1439-1447.

Characterization of Mesenchymal Stem Cells (MSC) quality during and after culture in stirred tank bioreactors for therapeutic purposes

By Melissa Porte, Study engineer

Supervisors: Isabelle Chevalot, Celine Loubière, Jessica Schiavi-Tritz

Keywords Mesenchymal Stem cells · Bioprocess · Flow cytometry · Control quality (CQ) · Bioreactor

BIOPROMO, CELLEASY

General context, scientific issue

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

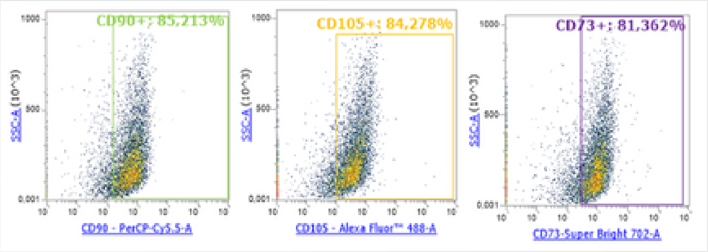
In this project, some of the objectives will be to carry out the quality controls of cells produced (1) in 2D in T-flasks and (2) in 3D on microcarriers suspended in a controlled and stirred bioreactor. For that, the biochemical and phenotypic aspects of the cells will be assessed throughout the culture 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 / Experimental approach

To control the quality of the cells in culture, flow cytometry tests are carried out to monitor and compare the phenotype between 2D and 3D modes. Target cells are labelled with antibodies coupled to fluorochromes, enabling them to be sorted according to their level of expression of different 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 express 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]

The important steps in achieving the present objectives are to grow the MSCs in 3D on plastic and soluble microcarriers, to monitor and improve their proliferation and finally to control the final product after culture. Undifferentiated, viable and active cells are expected for possible therapeutic applications.



Results of flow cytometry analysis of mesenchymal stem cells expressing their specific surface markers (CD90, CD105, CD73)

Main results

Currently, the culture of MSC in 2D and 3D on microcarriers in spinner flasks is controlled. High cell density, good cell viability and an expansion rate of between 10 and 15 within a few days have been achieved. In the near future, new microcarriers will be tested under optimal conditions and compared with results obtained using pre-selected microcarriers. Tests in agitated bioreactors will also be carried out, with phenotypic evaluation of the cells by flow cytometry at the start and end of culture.

An industrial partner (Restore) will carry out additional quality controls on cells cultivated in 3D system (differentiation test, sequencing, angiogenic potential test, etc.). These elements will enable to select the best microcarrier and the best culture conditions tested.

Finally, different culture media will be preselected by one of the project's partners (CellEasy) and tested under the growing conditions developed in the present study. The main objective is to cultivate MSCs in a medium without or limited amount 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.

References

[1] Zhou T, Yuan Z, Weng J, Pei D, Du X, He C, Lai P. Challenges and advances in clinical applications of mesenchymal stromal cells. J Hematol Oncol. 2021 Feb 12;14(1):24. doi: 10.1186/s13045-021-01037-x. PMID: 33579329; PMCID: PMC7880217.

[2] Gadelorge M, Bourdens M, Espagnolle N, Bardiaux C, Murrell J, Savary L, Ribaud S, Chaput B, Sensebé L. Clinical-scale expansion of adipose-derived stromal cells starting from stromal vascular fraction in a single-use bioreactor: proof of concept for autologous applications. J Tissue Eng Regen Med. 2018 Jan;12(1):129-141. doi: 10.1002/term.2377. Epub 2017 May 12. PMID: 27943660.

Innovative coupling of sensors integrated in bioprocesses for real-time monitoring of the physiological and metabolic status of eukaryotic cells

By Adèle Schini, 3rd year

Supervisors: Emmanuel Guedon, Bruno Ebel

Keywords
Bioprocesses
Spectroscopies
In situ sensors
CHO
Animal cell culture
Bioreactor
Optimization

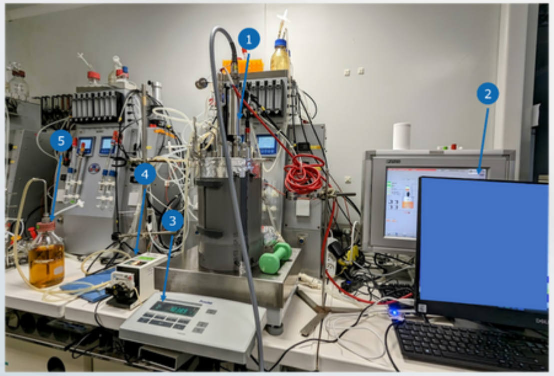
BIOPROMO,

General context, scientific issue

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.

Methodology / Experimental approach

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 cellular aspect and their metabolic state will be built. Several cell culture runs will be performed to assess the accuracy of the modeling approaches.



1: Bioreactor + spectroscopic sensors

2: Software for cell growth monitoring and pump control

3: Scale used to control nutrient addition

4: Controlled pump to add nutrient in the cell culture

5: Nutrient in solution (mainly glucose)

Illustration of a test bench for cell culture monitoring and optimization of cell growth thanks to feeding control.

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 thanks to an optimized and adapted process control.

Main results

Nine cell culture runs have been performed over these three years (6 batch and 3 fed-batch) and they allowed to determine the monitored parameters that can be used to control the glucose supply pumps in the bioreactor. The final modeling will give the user access to qualitative and quantative information about the current cell culture. Three cell cultures in fed-batch mode were carried out with controlled nutrient addition when the glucose concentration monitored on-line fell below a defined threshold. The aim is to reduce the threshold for nutrient addition as much as possible, in order to deliver a steady stream of glucose to the cells.

References

[1] Li M. 2018. Approche méthodologique innovante pour le suivi en ligne de procédés de production d'anticorps par cellules animales : apport des techniques spectroscopiques in situ à la stratégie PAT Thèse de doctorat soutenue le 09 Novembre 2018 à l'Université de Lorraine.
[2] Li M., Ebel B., Chauchard F., Guédon E & Marc A. (2019). Parallel comparison of in situ Raman and NIR spectroscopies to simultaneously measure mulple variables toward real- me monitoring of CHO cell bioreactor cultures. Biochemical Engineering Journal, 137, 205-213.
[3] Abu-Absi, N. R., Kenty, B. M., Cuellar, M. E., Borys, M. C., Sakhamuri, S., Strachan, D. J., Hausladen, M. C., & Li, Z. J. (2010). Real me monitoring of multiple parameters in mammalian cell culture bioreactors using an in-line Raman spectroscopy probe. Biotechnology and Bioengineering, 108 (5), 12151221. hps://doi.org/10.1002/bit.2302

Bioproduction project: Innovative Technology Solution for Micro/Mili Electrophoresis (IT'SME)

By Samuel Schneider, Study engineer

Supervisors: Laetitia Canabady-Rochelle, Christelle Mathé, Laurence Muhr

Keywords Chinese Ovary Hamster (CHO) Cell culture Bioreactor Harvest Bioprocess Monoclonal antibody IgG Microelectrophoresis Purification

BIOPROMO

General context, scientific issue

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.

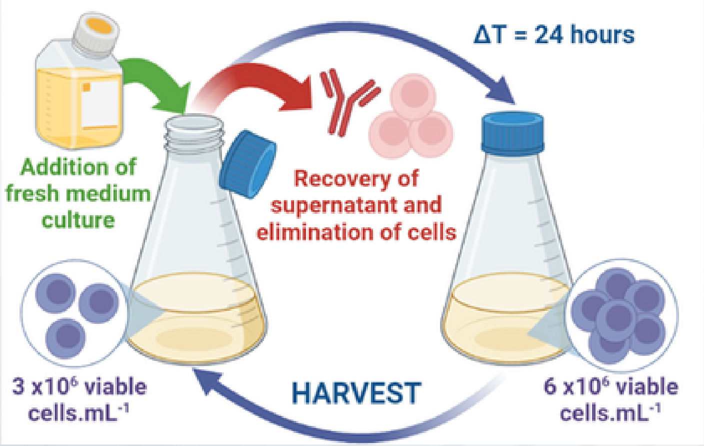
Methodology / Experimental approach

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 μFFEs to obtain the desired purity and comparison of the results with those obtained by conventional HPLC.



Description of the harvest culture in Erlenmeyer flask

Objectives and stakes

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.

Main results

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 perfused bioreactor culture.

References

[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. International Journal of Pharmaceutics 594, 120164. 10.1016/j.ijpharm.2020.120164.

[2] Beckmann, T.F., Krämer, O., Klausing, S., Heinrich, C., Thüte, T., Büntemeyer, H., Hoffrogge, R., and Noll, T. (2012). Effects of high passage cultivation on CHO cells: a global analysis. Appl Microbiol Biotechnol 94, 659–671. 10.1007/s00253-011-3806-1.

Figure created with BioRender.com

Optimization of human adipose derived stem cells culture in stirred tank reactor in order to scale-up to 50 L.

By Bastien Thauvin, 3rd year

Supervisors: Latifa Chebil, Eric Olmos, Julien Branchu, Camille Simon

Keywords Cell culture Microcarrier Bead-to-bead transfer Mesenchymal stem cells Bioreactor

BIOPROMO, EVERZOM

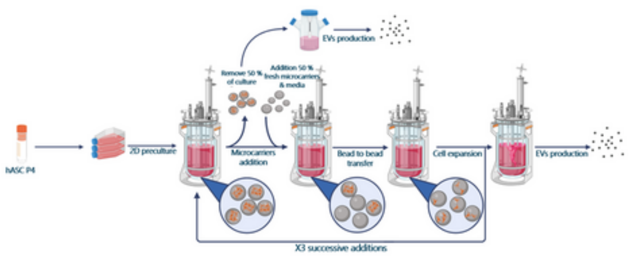
General context, scientific issue

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.

Methodology / Experimental approach

Human adipose derived stem cells (ADSCh) 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.

After each extraction and at the end of the culture, a production of EVs is carried out by stimulating the cells with turbulence. The suspension is then clarified, and the vesicles are characterized using nanoparticle tracking analysis and cytometry.



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

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.

Main results

Three 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 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 conserve minimal cell density to preserve cell growth. Finally, characterization of cells and EVs showed better EVs production of sequential production process with bead to bead than control batch without microcarrier additions. The identity has been verified and shows a signature comparable to the control process, with the presence of tetraspanins and MSC markers. 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.

References

[1] Dabrowska S et al. (2021) Immunomodulatory and Regenerative Effects of Mesenchymal Stem Cells and Extracellular Vesicles: Therapeutic Outlook for Inflammatory and Degenerative Diseases. Front. Immunol., Volume 11-2020.

[2] Gazeau F et al. (2018). Fluid system for producing extracellular vesicles and associated method (France. Patent No. WP 2019/002608 A1). WIPO. https://patentscope.wipo.int/search/ en/detail.jsf?docId=WO2019002608.

[3] Sion, C et al. (2021). A new perfusion mode of culture for WJ-MSCs expansion in a stirred and online monitored bioreactor.Biotechnology and Bioengineering, 118, 4453– 4464. https://doi.org/10.1002/bit.27914.

[4] Chen S et al. (2021). Facile bead-to-bead cell transfer method for serial subculture and large-scale expansion of human mesenchymal stem cells in bioreactors. Stem Cells Transl Med. 2021 Sep;10(9):1329-1342. doi: 10.1002/sctm.20-050.

Coupling of anaerobic dark fermentation and biomethanation for biomethane production

By Ludovic Vauthier, 2nd year

Supervisors: Stéphane Delaunay, Emmanuel Guedon, Emmanuel Rondags, Céline Loubière, Xavier Framboisier, Nakry Pen

Keywords Bioenergy Hydrogen Methane Microbial process Fermentation Bioconversion

BIOPROMO

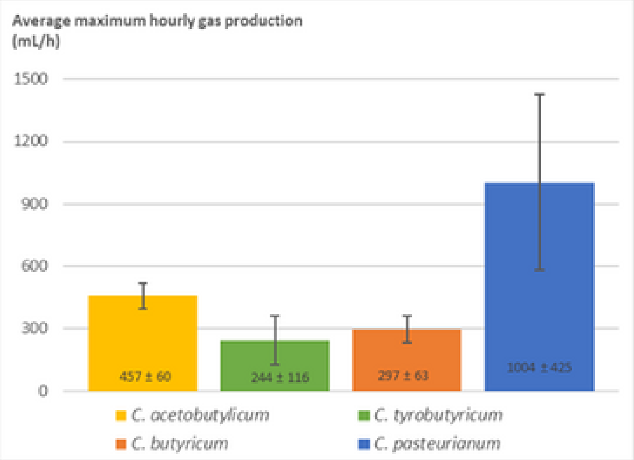
General context, scientific issue

The degradation of organic matter through anaerobic digestion results in a biogas composed by approximately 55% of CH_4 and 40% of CO_2, which is not energetic enough to be directly injected into the natural gas network. The aim of the present research is to convert the CO_2 into CH_4 to increase the methane content of the biogas.

Methodology / Experimental approach

- Firstly, 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. The ratio between H_2 and CO_2 in the biogas will also be evaluated. Multiple cultures will be necessary to make a statistical difference.
- Secondly, 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.
- Finally, the produced biogas will be transferred to another fermenter containing the microbial consortium from a digestate.

  It will be imperative 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 CO_2 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.



Comparison of gas productivity by several Clostridium strains

Objectives and stakes

To improve the CH_4 yield, two 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 H_2 will then be transferred to a microbial consortium (second process), for the bioconversion of CO_2 and H_2 into CH_4.

Main results

This year, multiple batch cultures were carried out under the same conditions (temperature = 37°C ; pH = 6 ; glucose concentration = 20 g/L) with 4 bacterial strains. Thanks to the acquisition of a micro-gas chromatograph for analytical measurements, the fractions of H_2 and CO_2 were precisely determined. The HPLC measurements are still used to evaluate the substrate consumption rate and the metabolites production. Statistically, C. pasteurianum was found to be the strain with the best H_2 productivity (twice more than C. acetobutylicum, three more time than C. butyricum and four more time than C. tyrobutyricum). Moreover, it has the highest specific growth rate, which is also a key parameter to move from batch to continuous cultures.

Continuous cultures are currently performed with C. pasteurianum in a 1L-bioreactor. 3 parameters (pH, substrate concentration and dilution rate) with 3 levels are considered in order to draw a Central Composite Design of Experiments. The future response surface of the outgoing H_2 flow will be our model to find the optimal conditions for the continuous H_2 production of our first process.

References

Aline Lebranchu (2017) 'Etude du procédé de méthanation en digesteur anaérobie à l'échelle pilote. Impact du mélange et du transfert gaz-liquide sur les performances de production de biogaz'. Université de Lorraine, 2017.

Simon Rittman and Christoph Herwig (2012) 'A Comprehensive and Quantitative Review of Dark Fermentative Biohydrogen Production'. Microbial Cell Factories 11 (1): 115. https://doi.org/10.1186/1475-2859-11-115.

Davis Rusmanis, Richard O'Shea, David M. Wall, and Jerry D. Murphy (2019) 'Biological Hydrogen Methanation Systems? An Overview of Design and Efficiency'. Bioengineered 10 (1): 604–34. https://doi.org/10.1080/21655979.2019.1684607.

Mohammad Javad Shaterzadeh & Seyed Ahmad Ataei (2017) 'The effects of temperature, initial pH, and glucose concentration on biohydrogen production from Clostridium acetobutylicum'. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 39:11, 1118-1123, DOI: 10.1080/15567036.2017.1297875

CITHERE

Kinetics Thermodynamics Energy

Biomass pyrolysis: advanced experiments and modeling

By Jana Alkoussa, 2nd year

Supervisors: Anthony Dufour, Julien Colin

Keywords Biomass Pyrolysis Bio-oil Biochar Fixed-bed reactor Laser Kinetic modeling

CITHERE

General context, scientific issue

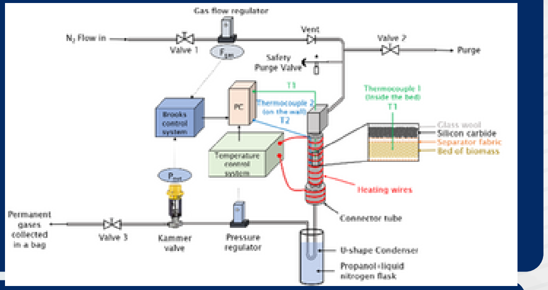
Fossil fuels have been a major source of energy for almost all aspects of our lives. They have supplied more than 80% of the total world's energy consumption which has increased rapidly due to population growth and industrial development. Consequently, to overcome the resulting concerns of climate change and the depletion of the global fossil fuels 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].

Methodology / Experimental approach

In the first part of the experimental work, 1 g of cellulose powder (PH-101~50 µm, 0.3 to 1g), either mixed or not with SiO_2 sand particles (600 to 850 µm), is pyrolyzed in a vertical cylindrical stainless-steel fixed bed reactor connected to a Kammer valve that allows the control of pressure (between 1 to 10 bars). This reactor is swept by N_2 with a flow rate varying between 20 and 200 mL/min. The reactor tube is heated with a slow heating rate (10°C/min) to the final temperature (320 to 400°C). Other experiments are realized using a new laser pyrolysis device (developed by G. Parent and S. Becker from LEMTA). A thin layer of cellulose or small particles of wood is laid over a graphite lamella that is heated by a powerful CO_2 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, and the volatiles are analyzed online by single photo-ionization mass spectrometry (SPI-MS).

Throughout the work, different characterization techniques are used to analyze the resulting products: µ-GC for permanent gases, GC-MS and NMR for bio-oils, as well as SEM and proximate and ultimate analysis for biochars.



Experimental setup of the pressurized fixed-bed reactor used for cellulose pyrolysis

Objectives and stakes

This study aims to unravel and model the mechanisms of biomass pyrolysis through advanced, well-controlled experiments conducted on real biomass particles and cellulose macromolecules. The first part of the research investigates the effects of pressure and sweep gas velocity on the composition and yields of products resulting from the pyrolysis of cellulose in a well-designed fixed-bed reactor. Studying the interplay between intermediate liquid-phase formation, the evaporation law, and mass transfer will also be conducted [3]. The second part focuses on biomass pyrolysis using a novel laser setup, enabling for the first time simultaneous online analysis of volatiles and imaging of temperature and particles. Moreover, the kinetics of cellulose pyrolysis will be modeled in collaboration with Prof. M. Garcia-Perez at Washington State University.

Main results

- A bibliographical review of different types of micro-reactors used for biomass pyrolysis has been done.
- Understanding the effect of pressure on cellulose pyrolysis is of great importance since the increase in pressure favors the formation of biochar [4]. In our case, a char yield of 42 wt% was obtained at 10 bars. Furthermore, increasing pressure promotes the dehydration reactions of cellulose.
- Due to the high thermal conductivity of graphite, a good homogeneity of the heating temperature is detected. This may enable us to overcome the problem of huge thermal lags present in most of the fast pyrolysis micro-reactors [5].
- The online analysis by SPI-MS combined with the laser device can be done effectively and softly. Since it dramatically reduces the fragment ions [6], it results in more interpretable mass spectra which helps in unraveling the chemical mechanisms during the biomass pyrolysis.

References

[1] Brosse N. et al., Biofuels Bioprod. Biorefining 2012, 6:580-598.
[2] Venderbosch R.H., John Wiley & Sons, Ltd 2019, 175-206.
[3] Dufour A. et al., A. Chem. Eng. Res. 2011, 89:2136-2146.
[4] Mok W. S.L. and Antal M.J., Thermochimica Acta 1983, 68:165-186.
[5] Prins M. J. et al., Energy Fuels 2009, 23:993-1006.
[6] Le Brech Y. et al., J. Anal. Appl. Pyrolysis 2016, 117:334-346.

Impact of various digestate thermochemical conversion processes on products

By Mohamed Aissaoui, (post-doctoral researcher)

Supervisors: Anthony Dufour

Keywords Pyrolysis Hydrothermal Gasification Biochar Digestates

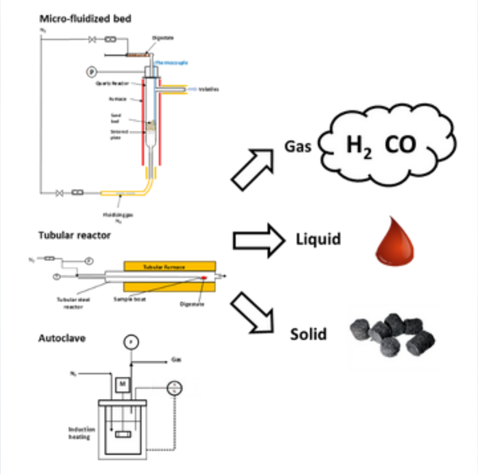
CITHERE

General context, scientific issue

Thermochemical conversion of digestates from methanization plants is an emerging topic aimed at increasing their value. Various methods such as hydrothermal conversion, pyrolysis, partial combustion, and steam-gasification were applied to convert agro-industrial waste digestates into chars, bio-oils, and gases. These processes were studied under different conditions to analyze the yield and composition of the produced materials, emphasizing the significant impact of temperature and reactive gases on the properties and chemical reactions of the products.

Methodology / Experimental approach

Raw digestates were converted: 1) by hydrothermal method in an autoclave equipped with a fast induction heating system to 250 and 300°C,2) by slow pyrolysis in a tubular reactor (at 10K/min) to 400°C, 600°C and 800°C final temperature with different residence times of the char at the final temperatures, 3) by fast pyrolysis, partial combustion and steam-gasification using a micro-fluidized bed reactor and operated under different fluidizing gas vectors (nitrogen, air and a mixture of steam and N2), reactor temperatures (from 400 °C to 900 °C). The mass yields of solids (char and ashes), syngas and liquids (bio-oils or tar) were quantified. The chars were analyzed by elemental analysis, XPS (for surface functional groups), ICP (for minerals) and BET (for specific surface area). The liquids were analyzed by GC/MS and high-resolution mass spectrometry (Fourier-transform ion cyclotron resonance, FT ICR MS). Gas composition was analysed by chromatography and FTIR (for NOx, NH3 and HCN).



Enhanced Value of Agro-Industrial Digestates via Thermochemical Conversion: A Comparison between Hydrothermal, Pyrolysis, Combustion, and Gasification Processes

Objectives and stakes

The main objectives of the study are 1) to increase the value of digestates from methanization plants through thermochemical conversion, 2) to produce a range of chars, bio-oils, and gases, as a function of various conversion methods and conditions (hydrothermal conversion, pyrolysis, partial combustion, and steam-gasification) 3) to investigate the influence of temperature, residence time, and reactive gases on the chemical reactions. Chars, liquids, and gases are characterized by using various analytical techniques (elemental analysis, XPS, ICP, BET, GC/MS, FT ICR MS, and chromatography) to understand their composition and potential applications.

Main results

The Van Krevelen diagram of char show the importance of dehydration and decarboxylation reactions on char composition. Steam presents a significant impact on the surface chemistry of chars leading to the formation of surface functional groups and increases the surface areas and pores volumes of the chars compared to pyrolysis and other process from 700 °C by physical activation2. For the XPS results, an interesting relation described between the H/C ratio and carbon yields over the wide range of pyrolysis conditions. Csp3 (in aromatic rings) are detected from 600°C and the N peaks become more structured and N is incorporated in Csp2. At 800°C, the pyrol groups are converted but they are more stable than pyridins. The oxygen surface moieties are well related with the fate of oxygen in the bulk3. All the oxygen atoms present in carboxyl groups clearly decrease with the temperature. Concerning minerals, HTL chars behave differently than pyrolysis chars due leaching of K and Na by the hot aqueous phase during hydrothermal conditions. The porous structure was determined by nitrogen and hydrogen sorption isotherms. Most of the micropores were not accessible to N2. The NLDFT surface increases with pyrolysis temperature up to 920m2/g at 800°C (slow pyrolysis). It is lower for fast pyrolysis at 800°C (420m2/g).

For the gas results, CO mass yield becomes higher for steam gasification than for pyrolysis from 800 °C, highlighting the significance of char gasification from 800 °C on CO formation. At 900°C, CO2 and CO present mass yields of 41 wt% and 26 wt%, respectively, for steam gasification. HCN formation is clearly evidenced from 500°C by the secondary conversion of nitrogen-containing aliphatic moieties formed by amino-acids pyrolysis4.
The GC/MS identifies a small fraction of organic liquid products only less than 1 wt%.db of the digestate mass but it clearly shows the important effect of air (O2) on the chemical reactions occurring in the free-board of the fluidized bed. The Principal component analysis of FT ICR MS data unravels the effect of air and steam on the composition of liquid products. Air promotes the formation of CHNO species whereas steam does not significantly impact the composition of the liquids (compared to pyrolysis) on the whole range of temperatures. At 900 °C, all liquids present a similar composition (based on FTICRMS analysis) highlighting the predominant effect of temperature than the reactive gas at 900 °C.

References

[1] Weber K, Quicker P. Properties of biochar. Fuel 2018;217:240–61. https://doi.org/10.1016/j.fuel.2017.12.054.
[2] Panwar NL, Pawar A. Influence of activation conditions on the physicochemical properties of activated biochar: a review. Biomass Conv Bioref 2022;12:925–47. https://doi.org/10.1007/s13399-020-00870-3
[3] Lahaye J, Nanse G, Fioux P, Bagreev A, Broshnik A, Strelko V. Chemical transformation during the carbonisation in air and the pyrolysis under argon of a vinylpyridine–divinylbenzene copolymer by X-ray photoelectron spectroscopy. Applied Surface Science 1999;147:153–74. https://doi.org/10.1016/S0169-4332(99)00108-7.
[4] Cao J-P, Li L-Y, Morishita K, Xiao X-B, Zhao X-Y, Wei X-Y, et al. Nitrogen transformations during fast pyrolysis of sewage sludge. Fuel 2013;104:1–6. https://doi.org/10.1016/j.fuel.2010.08.015.

Understanding the thermodynamic effects of reactive working fluids in thermodynamic cycles

By Aya Barakat, 3rd year PhD candidate

Supervisors: Jean-Noël Jaubert, Silvia Lasala

Keywords Chemical energy conversion | Chemically reactive working fluids | Reactive gaseous mixtures | Chemical equilibrium | Energy efficiency

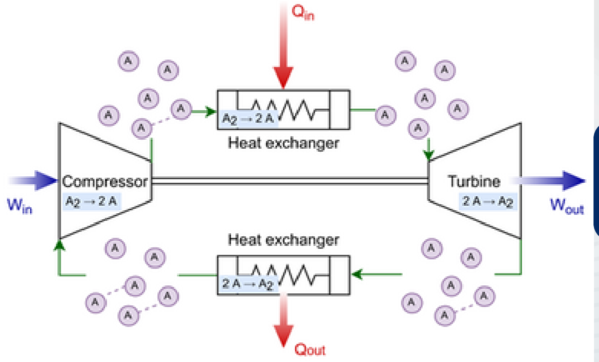
CITHERE

General context, scientific issue

As emissions regulations become stricter and environmental concerns grow, the need to improve the efficiency of energy converters has become more pressing. In this context, chemically reactive working fluids are being explored, moving away from the traditional inert counterparts. This allows the conversion of not only thermal energy–as is typical in conventional systems–but also chemical energy.

Methodology / Experimental approach

This work assesses a wide range of theoretical reactive gases, that are modeled as ideal gas mixtures, as candidate working fluids for different thermodynamic cycles. Each of the studied mixtures is based on the equilibrated chemical reaction: $A_{2(g)} \rightleftarrows 2A_{(g)}$
Where A is a theoretical ideal gas, and A2 is its dimer. Indeed, as the thermodynamic state (T,P) of the fluid changes due to transformations–such as compression, expansion, and heat exchange–within the cycle, the chemical reaction shifts towards a new equilibrium, leading to a new molar composition (molar fractions of A and A2). The reaction considered represents the dissociation and association of an ideal gaseous mixture, which enables the gas to be compressed in its associated form and expanded when dissociated, resulting in an improved net work of the cycle.
Each of the theoretical reactive gases studied is identified by a unique set of the reaction coordinates: the standard entropy change of reaction, , and the standard enthalpy change of reaction, .
Therefore, the reactive gases are investigated in Brayton [1], [2] and Stirling systems [3], considering both the forward and reverse cycles.
The behavior and properties of the fluids are assessed in each unit of the energy converters, and the overall performance is evaluated and benchmarked against that of comparable inert working fluids.



Dissociation and association reactions of a theoretical reactive gaseous mixture in a Brayton cycle

Objectives and stakes

The objective of this PhD is to understand the thermodynamic effects of utilizing chemically reactive working fluids, specifically in the gas phase, within thermodynamic cycles and processes. Therefore, the thesis aims to answer the following questions, among others: How does the reaction evolve during each thermodynamic transformation throughout the cycle? What are the effects of this chemical reaction on the fluid's composition and thermodynamic properties? What happens to the performance and net work of the cycle when utilizing reactive gaseous mixtures instead of inert gases?

Main results

When a reactive fluid undergoes a thermodynamic transformation, it experiences two effects due to the reaction. On one hand, the fluid's composition changes as the reaction shifts to a new equilibrium in response to changes in the thermodynamic state of the fluid. On the other hand, the exothermic or endothermic nature of the reaction affects the average kinetic energy, i.e., the temperature, of the fluid.
In a Brayton cycle, utilizing a reactive gaseous mixture results in more than a 140% increase in the net work output, compared to an inert system [1]. In a heat pump operating on the reverse Brayton cycle, results reveal a 212% increase in the coefficient of performance (COP) compared to an inert fluid system [2]. However, there is a trade-off between the system's COP and the mass flow rate required to maintain the same heat supply in Watts compared to an inert heat pump.
In the context of a Stirling cycle, it is observed that the use of reactive working fluids introduces irreversibility in the internal regenerator due to heat exchange across a finite temperature difference [3]. However, a slight increase of 5% in the net work output of a reactive Stirling engine is observed, without penalizing the thermal efficiency. On the other hand, for a reactive Stirling heat pump, it is observed that the exothermic reaction during compression significantly increases the thermal energy density per unit maximum volume by up to 269%, compared to an inert gas system.

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.ceja.2022.100400.
[3] A. Barakat, S. Lasala, P. Arpentinier, P. Tobaly, and J.-N. Jaubert, "Understanding the thermodynamic effects of chemically reactive working fluids in the Stirling engine," Energy Conversion and Management: X, p. 100573, Mar. 2024, doi: 10.1016/j.ecmx.2024.100573.

Development of an automatic generator of kinetic data for the oxidation stability of biofuels

By Gabriel Batalha De Souza, 2nd year

Supervisors: Baptiste Sirjean, René Fournet

Keywords Oxidation stability Biofuels Solvatation Kinetic models

CITHERE

General context, scientific issue

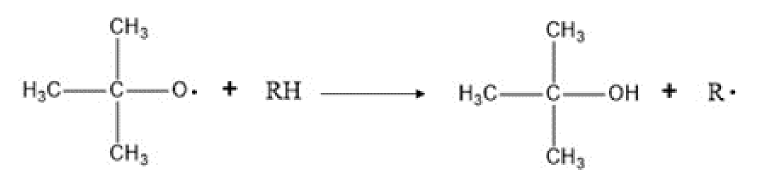
Currently, the combustion of fossil fuels is still the main source of energy used in several transport sectors, which is the main cause of global warming and the greenhouse effect. Therefore, biofuels would be an excellent alternative since they come from renewable sources and, in addition, the replacement 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].

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 the group.

Methodology / Experimental approach

Firstly, we theoretically studied the H-abstractions from five molecules by tBuO· (Figure 1): cyclohexane and toluene for validation of the methodology against experimental data, and cyclopentane, tetrahydrofuran and dioxolane. Potential energy surfaces were calculated at the CBS-QB3 and QCISD(T)/cc-PV∞QZ//B2PLYD3/6-311+G(2d,p) levels of theory. Hindered rotors were treated with the 1D-HR-U approach based on relaxed scans performed at the B3LYP/6-311G(d,p) for CBS-QB3 and B2PLYD3/6-311+G(2d,p) for QCISD(T)/cc-PV∞QZ.Quantum tunneling was taken into account with the Eckart method. The influence of Van der Waals complexes was probed using master equation/RRKM calculations with phase space theory for the barrierless formation of the complexes [2]. The potentials for the formation of pre- and post-reactive complexes were systematically fitted from relaxed scans between the centers of mass of each reactants or products at the B2PLYP-D3/6-311+G(2d,p) level of theory.



$$(CH_3)_3C{-}O\cdot + RH \longrightarrow (CH_3)_3C{-}OH + R\cdot$$

Figure 1. H-abstraction reaction of tBuO·

Main results

The rate constants calculated for the H-abstractions from cyclohexane and toluene by tBuO· agree with literature data as they lie within a factor of 1.3 (between 399 and 434 K) and 2.2 (at 299 K) of experimental data, respectively (Figure 2). We show that the pre-reactive complexes have a negligible effect on the computed rate constants from the results of master equation simulations without tunneling. However, our results show that the transmission coefficients need to be computed by explicitly including the pre-reactive complexes for more accurate results up to 700 K. The rate constant of the H-abstraction from cyclopentane is increased by a factor of 3 at 500 K when a CH2 group is replaced by an O-atom (THF). Replacing a second CH2 group by another O-atom (dioxolane) does not modify the total H-abstraction rate constant.

An Evans-Polanyi correlation is proposed and a linear relationship between the activation energy and enthalpy of reaction is observed for all cases excepted for toluene, which is the only molecule which leads to a resonance stabilized radical. Based on the computed data, it can be shown that that the hydrogen abstractions by tBuO· are entropy controlled (i.e., TΔS‡> ΔH‡).

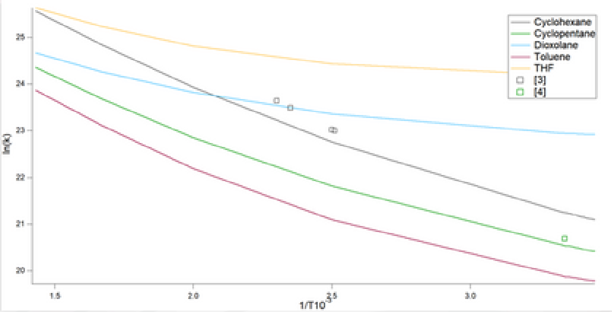


Figure 2. Kinetic rate constant of H-abstraction by tBuO·

References

[1] Westbrook, Charles K. "Biofuels combustion." Annual review of physical chemistry 64 (2013): 201-219.

[2] Georgievskii, Yuri, et al. "Reformulation and solution of the master equation for multiple-well chemical reactions." The Journal of Physical Chemistry A 117.46 (2013): 12146-12154.

[3] Sway, Mohammad I. "Kinetics of abstraction reactions of tert-butoxyl radicals with cyclohexane and methyl-substituted cyclohexanes in the gas phase." Journal of the Chemical Society, Faraday Transactions 87.14 (1991): 2157-2159.

[4] Li, S., & Fan, W. Y. (2006). FTIR and computational studies of gas-phase hydrogen atom abstraction kinetics by t-butoxy radical. Chemical physics letters, 427(4-6), 276-280

Effect of oxygen on the temperatures and conversion of tobacco in an electrically heated system

By Manon Bechikhi (engineer)

Supervisors: Anthony Dufour

Keywords Tobacco Electrically heated tobacco system Pyrolysis Oxidation Calorimetry

CITHERE

General context, scientific issue

The goal of Heated Tobacco Products (HTPs) is to devolatilize nicotine from the tobacco by a controlled electrical heating without inducing combustion and to thereby reduce the formation of harmful compounds typically related to self-sustained combustion of tobacco as in conventional cigarettes.

Objectives and stakes

The main objective of this work is to demonstrate the effect of oxygen under controlled thermal conditions relevant for HTPs. For this, we studied the temperature within the tobacco stick at different positions and under two different atmospheres: air and nitrogen. By using different analytical techniques, such as calorimetry, FTIR spectroscopy and principal component analysis (PCA), we can examine the impact of oxygen addition.

Main results

The temperature profiles are nearly identical for the two atmospheres showing only minor influences of oxygen (maximum temperatures: 318°C in air, 308°C in N2, at the end of the puffing cycle). The thermal degradation of the tobacco remains always globally endothermic due to high flow rate of the cold air flowing the tobacco during the puffing.

The residues are clearly differentiated by principal component analysis of the FTIR spectra, regardless of their radial positions in air or N2. This result highlights similar surface oxidation phenomena of the solid residue independent of position. The heating of the tobacco in the EHTS is relatively uniform along the electrically controlled heater without signs of local hot spots.

Calorimetric analyses evidence significant exothermic phenomena from about 230°C mainly due to gas-phase oxidation of primary volatiles in the hot gas stream. During the operation of the EHTS, such potential exothermicity is counter-balanced by strong heat losses and the high flow rate of cold air flowing through the tobacco bed during the puffing. Our study demonstrates that controlling the temperature in HTPs is essential to avoid combustion and the associated formation of harmful compounds.

References

[1] C.N. Uguna, C.E. Snape, ACS Omega 7 (2022) 22111-22124

[2] V. Cozzani, F. Barontini, T. McGrath, B. Mahler, M. Nordlund, M. Smith, et al. Thermochim. Acta 684 (2020), 178475

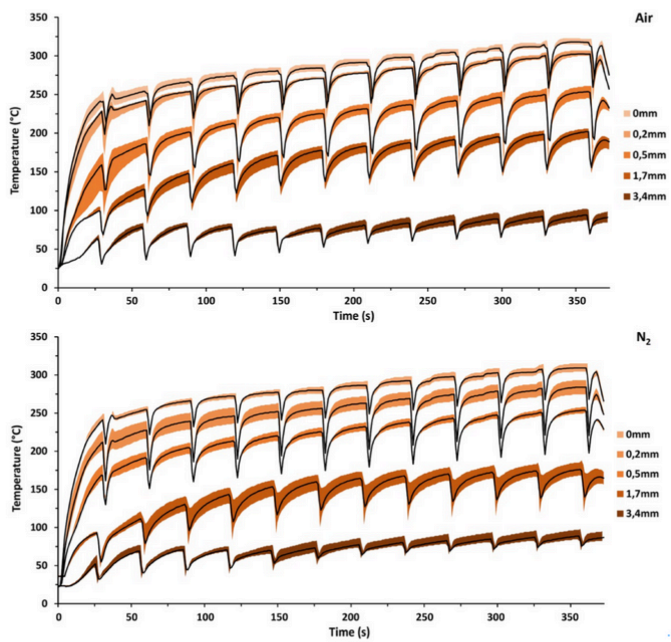
[3] M. Bechikhi, F. Quilès, R. Lainé, Y. Le Brech, A. Dufour, JAAP 177 (2024), 106312

Methodology / Experimental approach

In this study, we have instrumented a commercial puffing machine and an HTPs with a micro-positioning system of a thin thermocouple (0.25mm). The puffing was conducted under both nitrogen (N2) and air atmospheres. We provide the evolution of temperature as a function of time during standard puffing cycles and along the radial position within the tobacco plugs of tobacco sticks used as part of an electrically heated tobacco system (EHTS) during operation.

To better understand the differences between air and N2 puffing, we have imaged the solid residues collected in the tobacco plugs by FTIR spectroscopy. PCA was applied to FTIR spectra in the fingerprint spectral range of 1900-900 cm-1.

These experiments were also completed by calorimetry of tobacco upon pyrolysis or oxidation, in a 3D sensor and under a fixed bed configuration.



Comparison between temperature measured under Air and N2 at five different positions from the heater lamella: 0, 0.2, 0.5, 1.7 and 3.4 mm. The curve represents the average of 5 replicates, and the coloured region indicates the range between the maximum and minimum temperatures.

Experimental study of the impact of sustainable aviation fuels on the oxidation stability and combustion pollutants of fuels

By Ryma Benrabah, 3rd year

Supervisors: Baptiste Sirjean, Pierre-Alexandre Glaude

Keywords Sustainable aviation fuel (SAF) Liquid phase oxidation Microchannels Kinetic study In situ analytics Gas-liquid Taylor flow

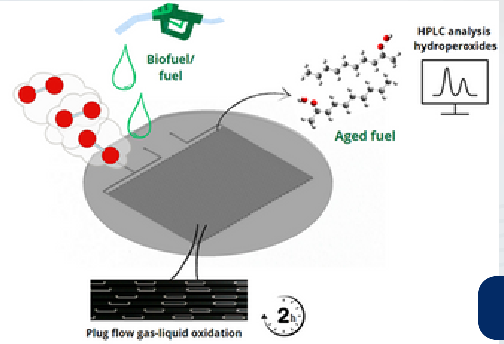
CITHERE, GCR

General context, scientific issue

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].

Methodology / Experimental approach

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 $A_{2(l)} \rightleftarrows 2A_{(g)}$ 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 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 I2 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. By comparing each method, we are able to determine the detection range of each technique.
Hydrodynamic and process conditions are studied for the microfluidic rig, PolyEtherEtherKetone-Autoxidation µChiped Heated Unit (PEEK-ACHU) to determine the optimal conditions for the oxidation pilot.



Overview of the experimental rig PEEK-ACHU

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).

Main results

Kinetics of a surrogate sustainable aviation fuel were studied at low extent of reaction using PEEK-ACHU.

This HPLC technique enabled the kinetic study of the oxidation of different surrogate fuels and a hydrodynamic study showed that since this difference between the two chromatograms in Figure 1 lies within the error of the analytical method, it can be concluded that the reaction is not limited by the mass transfer of oxygen in the liquid in the microreactor.

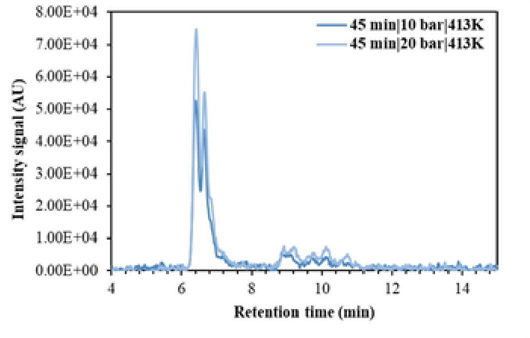


Figure 1: Hydroperoxide chromatograms obtained for n-decane autoxidation at two different pressures (10 and 20 bar) in PEEK-ACHU; at 413 K temperature and 45 min residence time

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

Innovative modelling methods to describe fluid properties

By Haziq Ridwan Bin Asmuni, 1st year

Supervisors: Jean-Noël Jaubert, Romain Privat

Keywords Equation of State EoS Association Association scheme

CITHERE, GTT

General context, scientific issue

SAFT-type model is one the EoS families known in thermodynamics. It takes into account different types of interactions at the fundamental level. One of the interactions is the association interaction, typically the hydrogen bonds. It can be seen in molecules possessing hydrogen acceptors and hydrogen donor sites such as alcohols, water, amines, carboxylic acids. This interaction is modelled by the association term which is a function of the number of non-bonded associating sites. It is determined from knowing the association scheme, usually selected empirically with a basic understanding of the structure of the molecule. Therefore, an additional term is to be determined which increase the number of parameters representing the molecule which in turn leads to a longer computational time.

However, in recent years, it has been observed that a well parameterized SAFT model without the association term can yield accurate results for associating compounds in particular for heavy compounds.[1]

Objectives and stakes

The objective of the PhD is to study the performance of SAFT-type models on different type of fluids. The following questions, amongst others, will be answered by the end of the thesis: do SAFT-type models perform better than cubic-type models in term of accuracy? Is the association term essential to model associative molecules? Which association scheme better represents a given functional group? Are the associative parameters transferable within the same function group?

Methodology / Experimental approach

PC-SAFT is chosen amongst many SAFT- family models. This choice does not influence the calculation of the association term. The latter is added on top of the dispersion and the hard chain terms. The association term which is a function of the non-bonded association site which in turn depends on the association scheme. The association scheme is chosen for a given functional group.

The previously constructed Fortran code is modified to take into account the association term. The latter can be calculated for any number and type of total sites on the molecule. The analytical expressions of the non-bonded sites are implemented.[2] An iterative calculation is performed the cases without the analytical expressions.

The isotherms in (P,V) plane are compared with commercial process simulator.

On the other hand, the non-associating PC-SAFT code is modified to implement the automatic differentiation using dual number.[3]

The final model will compare a wide range of molecules and produce a database for the PC-SAFT model parameters.

Main results

The association term is calculated for each association scheme. The different isotherms are compared to the PC-SAFT EoS from Aspen Properties and the obtained curves overlapped.

Contrary to the numerical differentiation which dependent to the perturbation, the accuracy of the automatic differentiation is independent on the step size of perturbation. In fact, the implementation of the automatic differentiation improved the accuracy of the derivatives which is comparable to the analytical differentiation. However, the computational speed decreased slightly when the number of the perturbations is increased.

References

[1] N. Ramírez-Vélez, R. Privat, A. Piña-Martinez, and J. Jaubert, ‘Assessing the performance of non-associating SAFT -type equations of state to reproduce vapor pressure, liquid density, enthalpy of vaporization, and liquid heat capacity data of 1800 pure fluids’, AIChE J., vol. 68, no. 7, p. e17722, Jul. 2022, doi: 10.1002/aic.17722.

[2] S. H. Huang and M. Radosz, ‘Equation of state for small, large, polydisperse, and associating molecules’, Ind. Eng. Chem. Res., vol. 29, no. 11, pp. 2284–2294, Nov. 1990, doi: 10.1021/ie00107a014.

[3] A. M. Aguirre-Mesa, M. J. Garcia, and H. Millwater, ‘MultiZ: A Library for Computation of High-order Derivatives Using Multicomplex or Multidual Numbers’, ACM Trans. Math. Softw., vol. 46, no. 3, pp. 1–30, Sep. 2020, doi: 10.1145/3378538.

Development of an automatic generator of kinetic models for the oxidation stability and combustion pollutants of sustainable biofuels

By Fabiola Citrangolo Destro, 3th year

Supervisors: Baptiste Sirjean, René Fournet

Keywords Kinetics | Automatic generation of rate constants | Transition state models | Ab initio calculations

CITHERE, ERC BIOSCOPE

General context, scientific issue

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].

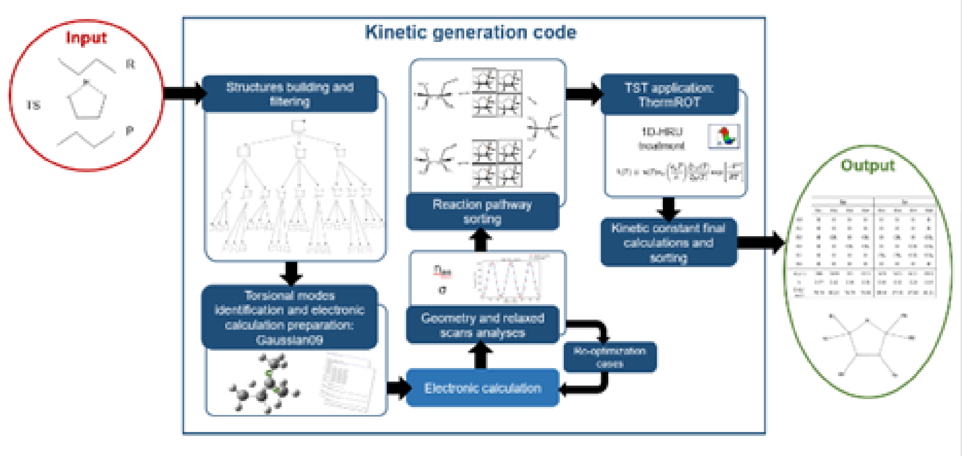
Objectives and stakes

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 / Experimental approach

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, including reactions passing through transition states with 4 and 5 members in the ring. A code in python was created and tested to expand the rate rules for generic TS. 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 data, and organizes them in a table that can be directly applied to reaction mechanisms. The kinetics of all the H-shift reactions of branched alkyls passing by 3, 4, 5 and 6 membered cycles were calculated and organized in the table. The code is also being applied for calculating the kinetics of beta-scissions and metathesis reactions.



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-membered cycle and 6-membered rings, as well as beta-scissions reactions. The results automatically produced were compared with previous manual results, and the code is found to outperform the human-produced kinetic data. The code is flexible to generate tables of TS models for other reactions classes, such as beta-scissions and H-abstractions.

References

[1] M. D. et al, J. Phys. Chem. B. 2021, 125: 6955-6967.
[2] R. van de Vijver et al., Int. J. Chem. Kinet. 2015, 47 :199–231.
[3] F. Citrangolo Destro et al., Proc. Combust. Inst. 2023,39:611-620.

Hydrothermal liquefaction of Moroccan two-phase olive mill wastes: effect of heating rate, reaction time and temperature

By Akram Dahdouh, Postdoc

Supervisors: Yann Le Brech, Anthony Dufour

Keywords Hydrothermal liquefaction | Olive mill wastes | Temperature | Heating rate

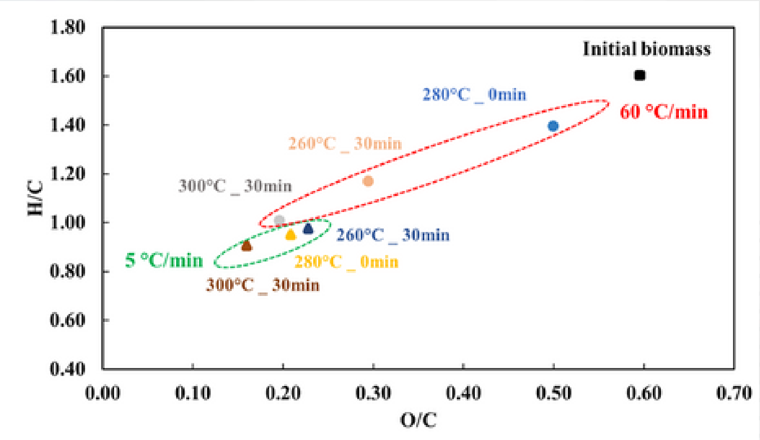
CITHERE, GREENER

General context, scientific issue

Olive oil industry generates annually huge amounts 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., 2023a). 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(Dahdouh et al., 2023b; Gimenez et al., 2020).

Methodology / Experimental approach

After the characterization of the raw biomass (volatile matter, ash content and fixed carbon, elemental analysis, FTIR spectra). Hydrothermal liquefaction (HTL) 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 and heating rate on the products yields and quality. The obtained products were analyzed with different techniques: Elemental analysis, Fourier transform infrared spectroscopy (FT-IR), and GC-FID/MS.



Van Krevelen diagram of hydrochars produced from fast and slow heating experiments

Objectives and stakes

The aim of this study is to investigate the effect of fast heating on the products distribution and properties during hydrothermal liquefaction of wet olive oil waste of Moroccan origin, two-phase olive mill waste. This work deals, first, with the characterization of the raw materials used, then with the understanding of the effect of the operating parameters (time, temperature, and heating rate). The resulting products (hydro-chars, biocrude, aqueous phase and gas) will be characterized by different techniques to identify the operating parameters effects on the products quality and composition.

Main results

This study highlighted the impact of reaction temperature and time on the hydrochars composition and quality. Results have shown that fast heating rate present different influences of reaction time and temperature on the product yields. The obtained results show that a fast-heating rate of 60 °C/min results in higher bio-oil yield and lower hydrochar yields compared to the slow heating rate (5 °C/min). Additionally, the reaction time effect is more apparent during fast heating experiments contrary to slow heating where no significant effect is observed. Moreover, heating rate variations have a significant effect on products quality. Indeed, as illustrated in Van Krevelen diagram, hydrochars from slow heating rate experiments present higher energy content indicating a higher degree of carbonization due to the higher residence time during the heating step.

References

Dahdouh, A., Khay, I., Le Brech, Y., El Maakoul, A., Bakhouya, M., 2023a. Olive oil industry: a review of waste stream composition, environmental impacts, and energy valorization paths. Environ. Sci. Pollut. Res. 30, 45473–45497. https://doi.org/10.1007/s11356-023-25867-z

Dahdouh, A., Le Brech, Y., Khay, I., El Maakoul, A., Bakhouya, M., 2023b. Hydrothermal liquefaction of Moroccan two-phase olive mill waste (alperujo): Parametric study and products characterizations. Ind. Crops Prod. 205, 117519. https://doi.org/10.1016/j.indcrop.2023.117519

Gimenez, M., Rodríguez, M., Montoro, L., Sardella, F., Rodríguez-Gutierrez, G., Monetta, P., Deiana, C., 2020. Two phase olive mill waste valorization. Hydrochar production and phenols extraction by hydrothermal carbonization. Biomass Bioenergy 143, 105875. https://doi.org/10.1016/j.biombioe.2020.105875

Combustion performances of biofuels resulting of Enzymatic Hydrolysis Lignin

By Nicolas Delort, 3rd year

Supervisors: Frédérique Battin-Leclerc, Olivier Herbinet

Keywords Biofuel Lignin Combustion Flame Modeling Oxygenated aromatics

CITHERE

General context, scientific issue

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 EHLCATHOL [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 / Experimental approach

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:

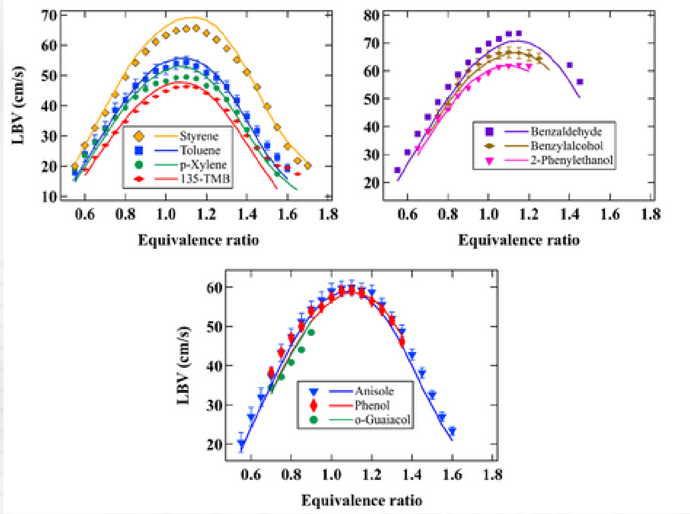
- LBV measurements with a flat flame burner at atmospheric pressure using the heat flux method [3]. Experiments are performed on a wide range of equivalence ratios for various fresh gas temperatures. This facility has been improved to face issues due this biofuel properties [4]; its main advantage is 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.

References

[1] International Energy Agency, (n.d.). https://www.iea.org (accessed April 4, 2022)
[2] http://ehlcathol.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.

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, phenyl radicals and of phenoxy-like and benzyl-like radicals, which are resonance stabilized, in the combustion process.



The COLIBRI model is also validated against the JSR results of Ismahane Meziane, the second PhD student involved in the project at LRGP who defended in December 2023, and on all the existing available literature data for the selected surrogate compounds of lignin derived biofuel.

Experimental study and kinetic modeling of the combustion of natural gas and biogas under oxy-combustion conditions

By Le Minh Dinh, 1st year

Supervisors: Olivier Herbinet, Frédérique Battin-Leclerc

Keywords Natural gas Biogas Oxy-combustion Jet-stirred reactor Decarbonization

CITHERE

General context, scientific issue

This PhD thesis is part of the program “Support innovation to develop new largely carbon-free industrial processes” supported by the French Government in the framework of the decarbonization of the industry to achieve carbon neutrality by 2050 [1]. The goal of this work is to provide better knowledge and skills in oxy-combustion for the optimization of eco-efficient processes [2] facilitating CO2 capture.

Methodology / Experimental approach

The first task will focus on the investigation of methane oxy-combustion in a jet-stirred reactor, which is considered an ideal system and is usually used in chemical gas phase kinetics because of its simple hydrodynamics enabling the decoupling of kinetics from physical phenomena. All experiments will be carried out over a wide range of temperatures (typically from 850 K to 1225 K), with an inlet mole fraction of CH4 fixed at 0.02. Three conditions, including fuel-lean, stochiometric, and fuel-rich mixtures, will be considered to study the effect of fuel-air equivalence ratios (). The pressure and residence time will be maintained at 800 torr and 2 s, respectively, while CO2 will be used as diluting gas for the first set of experiments. Further tests will be made with the addition of H2O (from 10% to 50%) in the diluent to study the effect of this species on the system reactivity and product selectivity. The mole fraction profiles of reactants and products are measured with gas chromatography, mass spectrometry, and FTIR spectroscopy. Some additional flame experiments will be performed in collaboration with an academic partner of the OXY3C consortium to enlarge the range of data needed for model improvement.

The second task will consist in using these experimental data for a more constrained capability test of different literature detailed kinetic models. Several models will be considered for a benchmark study. Selected models were built by recognized research teams for their contributions in kinetics (e.g., Politecnico di Milano – CRECK and University of Galway in Ireland – GALWAY). The chemistry of the model with the best performances will be improved thanks to deep kinetic analysis highlighting sensitive reactions and kinetic parameter benchmarking.

This work will provide a comprehensive database for oxy-fuel combustion of methane as well as a detailed kinetic model with updated chemistry for the prediction of methane oxidation under CO2-H2O dilution conditions.

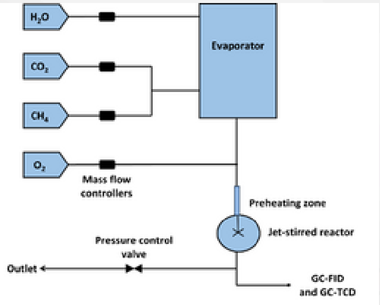
References

[1] https://www.pepr-spleen.fr/en/accueil-english/
[2] Bagheri G et al., Combustion and Flame 2020, 212:142–55.
[3] A. Stagni et al., Chemical Engineering Journal 2020, 385:123401.

Objectives and stakes

The objective of the thesis consists of both experimental works and simulations to improve the comprehension of the methane oxidation process under oxy-combustion conditions. Firstly, the oxidation of methane will be investigated at a laboratory scale to characterize the reactivity and the product distribution under CO2-diluted conditions. The influence of water on methane oxidation will be then investigated through experiments by considering CO2-H2O mixtures as diluent. A benchmarking of literature models will be performed to highlight their prediction capabilities under oxyfuel conditions. Kinetic analysis of models will be made to highlight sensitive reactions and propose an updated version of the methane oxidation chemistry.

Figure 1: Schematic diagram of the instrument



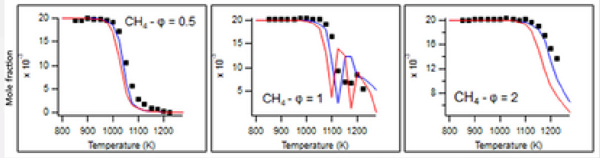


Figure 2: Experimental (symbols) and predicted (line) CH4 mole fraction profiles obtained during the combustion under CO2 dilution. Red lines: CRECK model; blue lines: GALWAY model

Main results

Figure 2 displays the experimental mole fraction of methane recorded under CO2 dilution. Methane is not reactive at temperatures below about 950K, and the leaner the mixture, the higher the reactivity. Products detected with gas chromatography are CO and C2 species. The GALWAY model seems to provide the best agreement for the reactivity, and the product mole fractions are overall well reproduced (not shown here), while the CRECK model over-estimates the reactivity. The main difference between the two models likely relies on the used sets of kinetic parameters. Strong oscillating behavior is predicted for temperatures above 1100 K in the stochiometric condition. The scattering in experimental mole fractions over this temperature range is thus likely due to these oscillations. A mass spectrometer with online sampling will be used to confirm their occurrence [3]. The addition of water at 10% has a very moderate effect on the reactivity and the product mole fractions. Experiments with higher water content will be performed to confirm this trend.

Recycling rare earths from mobile phone waste using deep eutectic solvent

By Guillaume Dumet, 1st year

Supervisors: Fabrice Mutelet, Jean-Charles Moïse

Keywords Rare earth elements (REE) Deep eutectic solvent (DES) Recycling Separation Liquid-liquid extraction

CITHERE

General context, scientific issue

Today, only 1% of the world's rare earths are recycled. However, reserves are gradually running out, while their use has exploded over the last 10 years. This can be explained by the fact that these elements are one of the most widely used resources in the energy transition (wind turbines, batteries...). Moreover, the currently developed methods often lack sufficient efficiency, are impractical for industrial-scale implementation, or involve multiple steps and the use of hazardous solvents[1] .

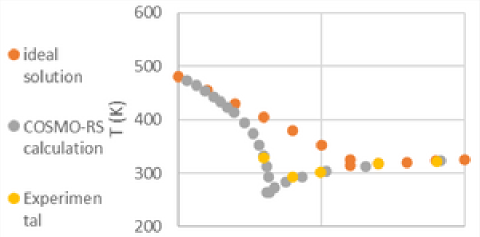
Methodology / Experimental approach

The search for new deep eutectic solvents is carried out using quantum chemistry and statistical thermodynamics calculations. The COSMO-RS model is used to verify that a selected binary system has a deep eutectic. These calculations are then validated experimentally by establishing the phase diagram of the system studied. Finally, a spectroscopic study is carried out to verify the presence of hydrogen bonds in the mixture. Then, a physico-chemical characterization (density, viscosity, TGA…) have to be carried out for these new solvents to ensure their compatibility in the process.

The second step is to determine the ability of the new DES to extract the RE present in an aqueous synthetic phase containing rare earth elements. The aim of this study is to optimize extraction yields by varying physico-chemical parameters of the process (pH, temperature, addition of a salt, etc.). This study will be complemented by a theoretical study to compare the extraction efficiency of these new DES with conventional deep eutectic solvents.

The last part of this study will be dedicated to the extraction of rare earths from various cell phone components. Phone magnets and vibrators will undergo thermal and mechanical treatment to obtain a powder containing rare earths and a few impurities (Fe, etc.). This fraction will then be treated either by direct leaching with DES or by dissolution followed by liquid-liquid extraction with DES. Each stage of the process will be studied to determine the optimum conditions and achieve the best recovery rate of RE. The most important parameter will be the ability of DES to extract rare earths while leaving impurities in the solid or aqueous phase.

In parallel with the experiments, predictive calculations were carried out to compare the affinity of rare earth chlorides and impurities with our new DES with those already listed in the literature but used in other extraction fields. These calculations give an idea of the optimum theoretical solvent to use for these extractions. These will be tested experimentally in order to obtain the most efficient and selective process possible.



Solid-liquid phase diagrams of one of the new DES: (yellow circle) experimentally; (grey circle) COSMO-RS predictions; (orange circle) ideal solubility line

Objectives and stakes

This study is devoted to the development of a separation process for recovering the rare earth elements (REE) from smartphone waste. One of the main objectives is to develop more efficient separation processes using environmentally-friendly solvents. Over the past decade, deep eutectic solvents (DES) have proven their performance in a wide range of industrial processes. These solvents, often based on natural products, are easy to synthesize, inexpensive and low in toxicity [2]. Moreover, these solvents can be easily recycled and reused that is minimized the amount of chemical product and the cost of process. One of the main objectives is to develop new deep eutectic solvents with suitable physico-chemical properties. These new family of solvents should also be capable of separating rare earths from impurities present in telephone waste.

Main results

Five new deep eutectic solvents have been identified and synthetized. Phase diagrams of binary systems were determined experimentally in order to confirm the presence of deep eutectic. Experimental data agrees well with solid-liquid equilibria predicted by COSMO- RS model. Physico-chemical characterizations were also conducted (density, viscosity, TGA, Karl-Fischer…). New DES exhibit hydrogen bonding and they present very high hydrophobicity. Their thermal stability, viscosity and density measured are not very high and are compatible with their use in liquid-liquid extraction processes.

Some extractions were carried out with these new solvents by varying the operating conditions. The best results were obtained with adding a salting agent to the aqueous phase. The extraction yield was close to 100% for each REs . One of them can extracted around 40 % of each REE but seem to be more selective for Lanthanum with only 20 % of extraction.

The aim now is to further optimize the extraction process by determining the extraction kinetics. Moreover, the action of salting agent is not clear so a spectroscopy study will be conducted to determine the exact mechanism during the liquid-liquid extraction.

References

[1]M. Danouche et al., « Advances in bio/chemical approaches for sustainable recycling and recovery of rare earth elements from secondary resources », Science of The Total Environment, vol. 912, p. 168811, févr. 2024, doi: 10.1016/j.scitotenv.2023.168811.

[2]M. Meenu et al., « Deep eutectic solvents (DESs) and natural deep eutectic solvents (NADESs): Designer solvents for green extraction of anthocyanin », Sustainable Chemistry and Pharmacy, vol. 34, p. 101168, sept. 2023, doi: 10.1016/j.scp.2023.101168.

Valorization of plastic waste and industrial bitumen by co-pyrolysis process

By Youssef Ech’chalh, 1st year

Supervisors: Raymond Michels, Valérie Vitzthum

Keywords Pyrolysis Co-pyrolysis Bitumen Plastic waste Asphalt Synergy Thermochemical recycling

CITHERE, GRÉSTOCK

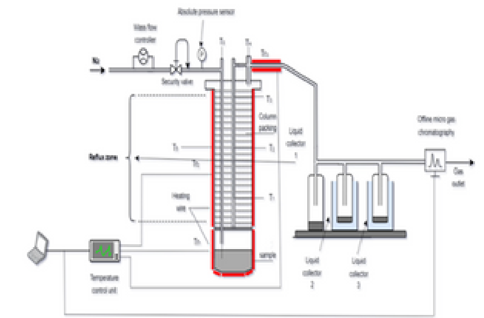
General context, scientific issue

The co-pyrolysis is a promising approach to exploit two (or more) types of materials in a synergistic way. By combining plastic waste with industrial bitumen, we seek to maximize the efficient use of these materials while reducing the environmental footprint associated with their disposal. Co-pyrolysis offers the possibility of recovering liquid hydrocarbons from these materials, which can be used as fuels or chemical feed stocks. The quality and quantity of products obtained by the co-pyrolysis depends on various experimental factors such as the type of plastic, reactor type, mass ratio and pressure.

This approach is in the context of finding sustainable solutions for the management of plastic waste and the search for alternative sources of hydrocarbons, thus contributing to the reduction of dependence on fossil resources.

Methodology / Experimental approach

The methodology of the thesis involves a series of experiments aimed at comprehending the reciprocal influence of plastic and industrial bitumen decomposition via co-pyrolysis. These experiments are conducted in two types of reactors (batch and semi-batch), heated to 480°C, and subjected to a wide pressure range (1 to a few hundred bars). Polypropylene and polystyrene plastics are utilized with varying bitumen to plastic mass ratios. Co-pyrolysis products are analyzed using online micro-GC for gases like H_2 and C1-C4, GC-MS/FID for pyrolytic oil (hydrocarbons >C6). So far, the pyrolysis of polypropylene (PP) has been explored using a semi-batch, vertical glass reactor heated to 480°C equipped with a reflux condenser heated at 200°C. Various heating rates were applied, and nitrogen served as the carrier gas with a flow rate of 100 mL/min.



Scheme of the reflux co-pyrolysis system of bitumen/polypropylene

Objectives and stakes

Given that bitumen has a lower cracking temperature compared to plastics, co-pyrolysis of bitumen and plastics is anticipated to reduce the cracking temperature of the mixture, while improving both quantity and quality of the oil produced due to the high Hydrogen/Carbone ratio of some plastics (Polypropylene in our case).

The research on co-pyrolysis of bitumen and plastics remains limited, therefore, this thesis aims to expand knowledge on how the decomposition of plastics and bitumen interacts synergistically in various reactor types and under various experimental conditions, such as different plastic-to-bitumen mass ratios, with a specific focus on the role of pressure to improve the oil yield.

Main results

The experimental work of this thesis began in February 2024 and very few results have been obtained so far.

References

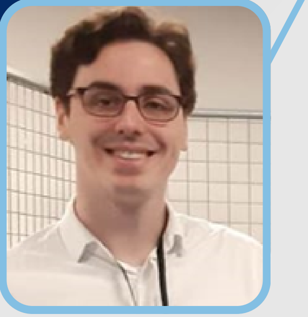
[1] M. Maniscalco et al., Experimental study of the pyrolysis of waste bitumen for oil production, Journal of the Energy Institute, 10 August 2020.
[2] H. Zhao et al., Thermal characteristics of bitumen pyrolysis. J Therm Anal Calorim (2012) 107:541–547.
[3] N. Hassibi et al., Analysis and control of 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, 12/14/2022.
[4] N. Hassibi et al., Thermochemical Recycling of Polystyrene by Pyrolysis: Importance of the Reflux to Maximize the Production of Styrene and BTEX, Industrial & Engineering Chemistry Research, 22/08/2023.

Kinetic modelling of the impact of oxygenated fuels on pollutant emissions in spark ignition engines

By Timothée Fages, 3rd year

Supervisors: Pierre-Alexandre Glaude, René Fournet

Keywords Gasoline Soot Biofuels Kinetic mechanism Combustion



CITHERE

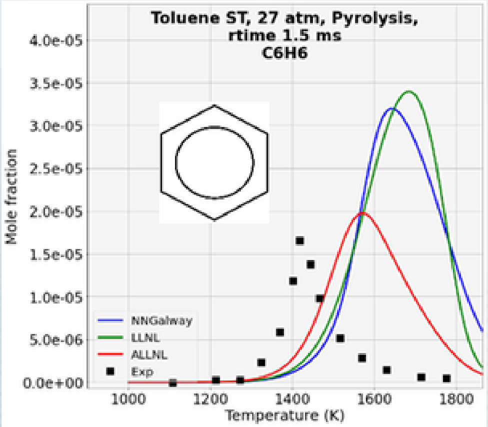
General context, scientific issue

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

Methodology / Experimental approach

The oxygenated gasoline is modeled with isooctane, n-heptane, toluene and either ethanol or isobutanol to make it computationally usable.
Different kinetic models from the literature were 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



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

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, NOx and soot precursors (polycyclic aromatic hydrocarbons - PAH).

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, is 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

Study of biochar composition as a function of various parameters

By Marilyne Farhat, 1st year

Supervisors: Anthony Dufour, Yann Le Brech

Keywords Biomass Pyrolysis Biochar Characterization

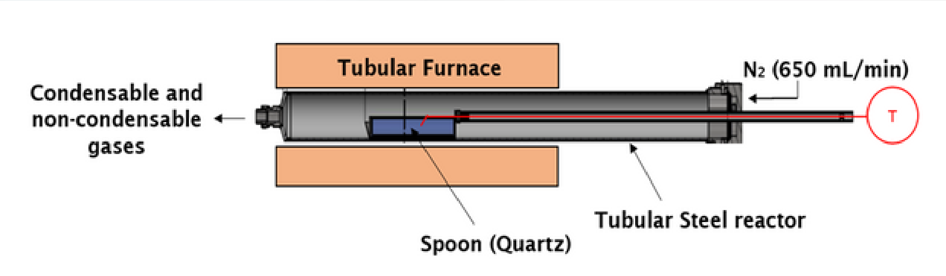
CITHERE

General context, scientific issue

The increasing energy demand and the rise in greenhouse gas emissions due to the overexploitation of fossil resources make research on renewable resources one of the most crucial challenges for humanity. Therefore, studies have progressed towards other alternatives, such as the conversion of biomass (wood, agricultural waste, digestates, manure) through pyrolysis. This process leads to the formation of biochars, bio-oils and permanent gases, each having characteristics that allow them to play vital roles in the energy sector. Biochar, containing a high percentage of carbon (>80%), has a wide range of applications (amendments, adsorbent, catalysts)1,2. The composition and properties of biochars are determined by the operating conditions of the raw material3 and the production process (type of pyrolysis, temperature).

Methodology / Experimental approach

Slow (10°C/min) and fast (1°C/s) pyrolysis of six biomasses (Oak, Douglas, Corn cobs, Digestate, Cattle manure and Poultry droppings) were conducted in tubular reactors under nitrogen at two temperatures (550 and 700°C). The structure and composition of the produced biochars were studied using various characterization techniques (Elemental analysis, Thermogravimetric analysis (TGA), Muffle furnace, Inductively Coupled Plasma (ICP), X-Ray Fluorescence Spectroscopy (XRF), Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDX)).



Scheme of the experimental setup

Objectives and stakes

The objective of this study is to conduct pyrolysis of various biomasses (lignocellulosic and non-lignocellulosic), under different pyrolysis conditions (slow and fast) and at different temperatures (550 and 700°C), producing batches of biochars whose structure and composition will be studied using various characterization techniques, aiming to understand the influence of these different parameters on the obtained product.

In a second phase, the various characterization techniques will be compared to select the most suitable ones that will allow for achieving a 100% material balance.

Main results

The results showed that biochar yields decrease with rising temperatures and are higher following the pyrolysis of non-lignocellulosic biomass rich in minerals.

On the other hand, increasing the pyrolysis temperature leads to higher percentages of carbon, fixed carbon and ash in the biochars, but a decrease in the percentage of volatile matter.

In addition, biochars derived from non-lignocellulosic biomass contain less carbon and fixed carbon than those derived from lignocellulosic biomass, but more volatile matter and ash.

References

[1] Haghighi Mood, S. et al. Perspectives of Engineered Biochar for Environmental Applications: A Review. Energy Fuels 2022, 36 (15), 7940–7986.

[2] Daful, A. G.; R Chandraratne, M. Biochar Production From Biomass Waste-Derived Material. In Encyclopedia of Renewable and Sustainable Materials; Elsevier, 2020; pp 370–378.

[3] Weber, K.; Quicker, P. Properties of Biochar. Fuel 2018, 217, 240–261.

Molecular design of reactive working fluids for thermodynamic cycles

By Rachid Hadjadj, post-doctoral researcher

Supervisors: Silvia Lasala

Keywords Reactive fluids Thermodynamic cycles Molecular design Computational calculations Enthalpy of reactions

CITHERE

General context, scientific issue

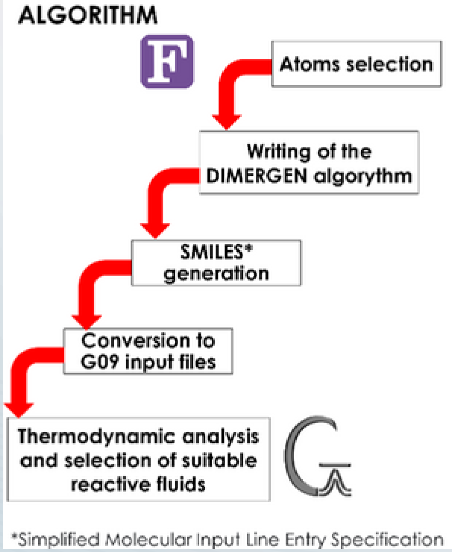
To face the increasing energy demands and environmental concerns, the development of efficient and sustainable energy conversion technologies such as thermal power plants, refrigerators and heat pumps is crucial [1,2,3].

Methodology / Experimental approach

To achieve this goal, a predefined workflow has been followed (Figure 1). A script able to generate all possible monomer/dimer molecules A/A2 from preselected set of atoms has been developed (called DIMERGEN) in the Fortran programming language. A list of reactions has been obtained for their subsequent thermodynamic characterization.

Quantum Chemistry calculations using the Gaussian 09 program package have been performed on the monomers and dimers using the CBS-QB3 method [4] to predict thermochemical properties such as the enthalpy and entropy of the reaction, and its kinetics.

This will allow us to evaluate the performance of the selected fluids in the considered applications, under various conditions, and estimate their potential for energy conversion.



Workflow for the generation and thermodynamic analysis of reactive fluids.

Objectives and stakes

Exploiting the chemical energy of reacting fluids instead of inert ones in the thermodynamic cycles might be an excellent way to significantly increase the efficiency of thermal conversion technologies. In this work, we propose an innovative approach to construct and select reactive fluids to be used in thermodynamic cycles. We have focused in the generation of dimer molecules following the reversible chemical reaction of $A_2 = 2A$ (A being a monomer).

Main results

The DIMERGEN Fortran code was designed to generate reactive fluids in several lists. Each list represents a family of molecules. Each family has central atoms with the same valence number and type of bonding.

The main results are the following:

1. The DIMERGEN Fortran code was able to generate about 500 dimers (which equals the number of reactions) classified in 23 lists (families) according to certain criteria.
2. After performing quantum chemistry calculations, we noticed that a hundred of dimers were stable, reducing the number of families to 17 families. All these dimers, the corresponding monomers, and thus the full reaction have been fully characterized from a thermochemical point of view.
3. The kinetic analysis of all the reactions showed that among these stable reactions, about half are considered as fast and reversible in the applications of our interest.
4. Validation of the theoretical results have been made and the results have been judged to be satisfactory.

References

[1] S. Lasala, R. Privat, O. Herbinet, P. Arpentinier, D. Bonalumi, and J.-N. Jaubert. (2021), Thermo-chemical engines: Unexploited high-potential energy converters, Energy Conversion and Management, vol 299, 113685

[2] A. Barakat, S. Lasala, P. Arpentinier, and J.N. Jaubert (2022), The original and impactful exploitation of chemical energy in heat pumps, Chemical Engineering Journal Advances, vol 12. 100400

[3] Website of the project REACHER: https://www.univ-lorraine.fr/erc-reacher/

[4] J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, A complete basis set model chemistry. VII. Use of the minimum population localization method, J. Chem. Phys., 112 (2000) 6532-42. DOI: 10.1063/1.481224

Valorization of products derived from the hydrothermal conversion of olive oil waste

By Boutaina Illoussamen, 2nd year

Supervisors: Fabrice Mutelet, Yann Le brech

Keywords Olive oil waste Hydrothermal conversion Phenolic compounds Deep eutectic solvents

CITHERE

General context, scientific issue

Olive oil production generates over 30 million m³ of waste annually, including solid (olive pomace), semi-solid (olive mill waste) and liquid (olive mill wastewater) byproducts (Dahdouh et al., 2023). Without effective treatment, these byproducts pose serious environmental risks due to their high phenol content, acidity, and organic load. In response, this thesis project explores two main valorization pathways:

Energetic Approach: Transforming wastes into bio-oils and hydro-char through hydrothermal conversion.

Extraction Process Optimization: Recovering high-value phenolic compounds from olive oil waste using deep eutectic solvents

Methodology / Experimental approach

Characterization of Olive Mill Wastewater: the characterization of olive mill wastewater was performed using various experimental techniques to understand its composition and properties (UV-Vis Spectroscopy, fluorescence Spectroscopy Measurement, Total Phenolic and Flavonoid Content, Total Organic Carbon (TOC), FTIR Spectroscopy and HPLC-MS.

Screening and Selection of Deep Eutectic Solvents (DES): over 65 hydrophobic DES were screened using the COSMO-RS model to identify the most effective solvents for extracting phenolic compounds from olive mill wastewater.

Liquid-Liquid Extraction Process: a specified amount of olive waste was placed into glass cells and mixed with a precise volume of DES. The mixture was stirred at a constant temperature under atmospheric pressure for 12 hours. Followed by a 12-hour rest period for phase separation.

Quantification and Identification: after separation, the aqueous phase was analyzed for phenolic compounds using the Folin–Ciocalteu method. Extracted compounds were identified and quantified by Liquid Chromatography-Mass Spectrometry (LC-MS/MS).

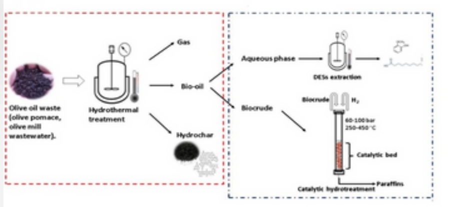
Parametric Analysis of Hydrothermal Conversion: a parametric analysis of the hydrothermal conversion of olive oil waste will be conducted, focusing on operational parameters such as time and temperature. The products of this process (hydro-char, aqueous phase, and gas) will be characterized using various techniques to determine how these parameters influence the production and extraction of phenolic compounds.

Comparison of Extraction Efficiencies: The study will compare the extraction efficiency of phenolic compounds from olive mill wastewater before and after hydrothermal treatment. This comparison aims to identify the most effective method for maximizing phenolic compound recovery and optimizing the valorization process.

Objectives and stakes

The aim of this study is to develop extraction process using new class of solvents to recover the polyphenolic substances from the olive oil waste of Moroccan origin. A theoretical study based on the COSMO-RS model was carried out to define the most efficient deep eutectic solvents for extracting phenolic compounds. This work is also devoted to the characterization of the raw materials used and the influence of the operating parameters (organic/aqueous phase mass ratio, kinetics and temperature) on the extraction efficiency of phenolic compounds from raw olive wastes using deep eutectic solvents.

Additionally, the study will conduct a parametric analysis of hydrothermal conversion focusing on time and temperature, characterize the resulting products, and compare the extraction efficiency of phenolic compounds from olive mill wastewater before and after hydrothermal treatment focusing on the aqueous phase obtained after hydrothermal treatment. This comprehensive approach aims to develop sustainable and efficient methods for managing and valorizing olive oil waste.



Global approach of the thesis project

Main results

A bibliographical study was carried out on hydrothermal conversion and extraction conditions of various agricultural wastes. This study revealed a lack of research work focusing specifically on the extraction process of the aqueous phase resulting from the hydrothermal conversion of olive waste. In addition, only a limited number of articles have addressed the hydrothermal conversion of olive oil waste. These results underline the importance of studying the coupling between the liquid extraction process and the hydrothermal energy recovery of olive oil waste.

The extraction efficiency of these valuable compounds using four deep eutectic solvents from olive mill waste water and olive pomace was carried out.

Results of the liquid-liquid extraction have shown that the extraction process requires less than 5 min with high yields (more than 75%). Temperature has a minimal impact while the organic/aqueous phase mass ratio has an important effect on the efficiency. LC-MS analysis demonstrated that deep eutectic solvents are able to extract numerous phenolic compounds from olive oil waste.

References

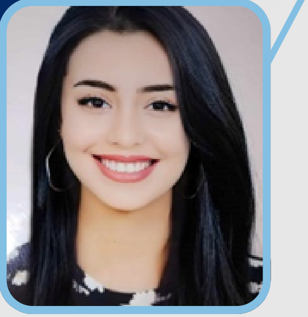
[1] Dahdouh, A., Khay, I., Le Brech, Y., El Maakoul, A., & Bakhouya, M. (2023). Olive oil industry: a review of waste stream composition, environmental impacts, and energy valorization paths. Environmental Science and Pollution Research, 30(16), 45473-45497.

Sustainable management of lignocellulosic and plastic waste: combating climate change and developing the circular economy

By Syrine Jouini, 2nd year

Supervisors: Aida Ben Hassen Trabelsi, Guillain Mauviel

Keywords Waste management | Plastic waste | Circular economy



CITHERE, LMVEED

General context, scientific issue

We are living with a global dependence on plastic polymers because of their versatility, low density, durability and low production cost compared to other materials. As a result, the production of plastic waste has increased: in 2020, more than 400 million tons of plastics per year were produced worldwide. However, plastic waste management technologies such as landfilling, incineration and mechanical recycling are not perfect, because of the leaching of toxins into the soil and groundwater, greenhouse gas emissions and the disruption to infrastructure and the selectivity of plastic waste in the recycling sector. As a result, energy recovery through thermochemical conversion, specifically pyrolysis, is the alternative that not only reduces the environmental impact of these polymers by minimizing pollution, but also offers new opportunities for sustainable socio-economic development in many sectors.

Methodology / Experimental approach

We will initially begin by carefully preparing the samples, by collecting and initially characterizing the waste to be studied (PS, PP, PVC, HDPE, LDPE), followed by the preparation of mixtures according to a defined experimental plan. The pyrolysis experiments will then be carried out in a Pyrex semi-batch tubular reactor, with rigorous control of the reaction parameters.

The pyrolysis products (gas, char and oil) will be collected and subjected to in-depth characterization, including gas analysis by gas chromatography (GC), char analysis by proximate analysis and CHNS, and oil analysis by GC-MS, 1H NMR and DSC. The experimental data thus obtained will then be subjected to statistical analysis and empirical modelling using artificial intelligence techniques, specifically artificial neural networks, to predict the yield of pyrolysis products and their composition as a function of waste characteristics and pyrolysis conditions. Finally, the results will be interpreted to identify the relationships between pyrolysis parameters, waste composition and pyrolysis products, with recommendations made for optimising the pyrolysis process or the use of the products obtained.

Photo of the pyrolysis system with a reflux zone

Objectives and stakes

The first objective is to pyrolyze waste streams of various kinds - that cannot be recovered by mechanical recycling - for the production of liquid, solid (char) and gaseous (syngas) products. I entend to focus on the problem of the link between pyrolytic behavior and the physico-chemical characterization of varied and more or less complex solid fuels. This would allow defining a methodology enabling a manufacturer / design office to predict the pyrolytic behavior of a fuel (simple or complex) on the basis of a few physico-chemical analyses.

Main results

The results of this study would provide an in-depth view of the waste studied, highlighting its physico-chemical characteristics through detailed characterization. By identifying the optimum pyrolysis conditions, we could maximize yields of the desired products while minimizing undesirable by-products. In-depth analyses of the gases, char and oil produced would reveal their composition and application potential, while the predictive models developed would make it possible to anticipate yields as a function of reaction variables. These results would open up prospects for various applications, such as energy , chemicals and char production. In addition, an environmental impact assessment would offer insight into the potential benefits in terms of reduced greenhouse gas emissions and more efficient waste management, thus contributing to better resource management and more sustainable industrial practices. In addition, it could pave the way for new methods of recovering materials and producing energy from plastic pyrolysis products, thereby contributing to a more sustainable circular economy.

References

[1] Nabil H et al., Journal of Analytical and Applied Pyrolysis. 2023.

[2] Ben Hassen Trabelsi,A et al., WASTE AND BIOMASS MANAGEMENT IN TUNISIA: CURRENT SITUATION AND OPPORTUNITIES FOR RENEWABLE FUELS PRODUCTION. Venice 2020 / 8th international symposium on energy from biomass and waste / 16-19 nov 2020

High-throughput thermodynamic methods combined with oxidation stability models

By Francisco Paes, 3rd year

Supervisors: Romain Privat, Baptiste Sirjean, Jean-Noël Jaubert

Keywords Kinetic modeling Equation of state Solvation properties

CITHERE

General context, scientific issue

Automatic kinetic mechanism generators used in detailed kinetic modeling of oxidation processes can provide reliable thermo-kinetic data in ideal gas phase only. High-throughput thermodynamic models are therefore required to adapt this data into liquid or supercritical mediums.

Objectives and stakes

The objective of this work is to propose a flexible framework to correct the ideal gas thermo-kinetic data to liquid and supercritical solvents by means of a predictive version of a cubic equation of state (EoS). The role of the corrections is to incorporate solvation effects into the kinetic model. These effects arise from the molecular interactions established between solute and solvent molecules [1].

Methodology / Experimental approach

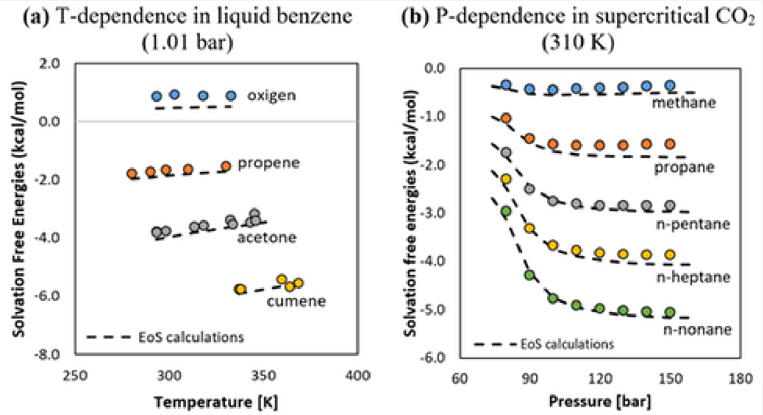
The aforementioned corrections are based on the solvation free energy (of solutes in the bulk phases. For a given temperature (), pressure () and composition (), can be calculated as follows:

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

This approach relies on the calculation of the fugacity coefficient of solutes (, along with the estimation of the molar volume of sovents (). Both can be straightforwardly estimated by a cubic EoS. In this study, a cubic EoS previously developed in our group was used: the tc-PR EoS (translated-consistent Peng-Robinson) [2]. The tc-PR is defined as follows:

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

The attractive parameter ( ), the co-volume (), and the volume translation (), are calculated based on the critical temperature (), critical pressure () and acentric factor () of molecules, or by a group contribution method previously developed. In this version, machine learning models (ML) based on molecular descriptors were used.
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 model (COSMO-RS [4]), was chosen to calculate the activity coefficients, which was also parametrized through a ML model.



Examples of parity plots for the prediction of solvation free energies in liquids and supercritical fluids.

Main results

The proposed equation of state demonstrates remarkable accuracy and versatility in predicting solvation data for any molecule across various solvent phases, including both liquid and supercritical states. By leveraging machine learning models to derive pure component data and activity coefficients with COSMO-RS, the need for experimental data and fitted binary interaction parameters (BIPs), commonly present in other equations of state, is eliminated.
The proposed model autonomously captures the temperature dependence of solvation free energies in liquid phase, as evidenced in the examples of Figure (a). In the realm of supercritical solvents, where solvation energies become pressure-dependent, the model adeptly accounts for this effect, as shown in Figure (b).

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.
[4] A. Klamt, F. Eckert, W. Arlt, , Annu. Rev. Chem. Biomol. Eng. 1 (2010) 101–122.

Optimization of the architecture of thermodynamic cycles operating with reactive fluids

By Luis Angel Pinilla Monsalve, 1st year

Supervisors: Silvia Lasala, Jean-Noël Jaubert

Keywords Thermodynamics Reactive fluids Optimization Thermal energy conversion

CITHERE

General context, scientific issue

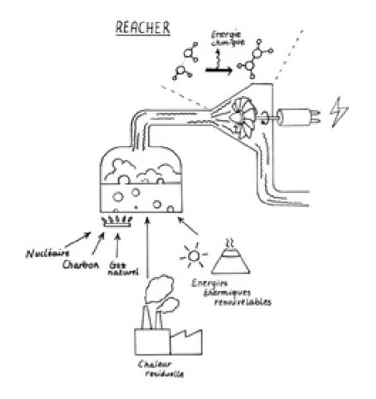
Energy transition is undoubtedly one of the main concerns of our society. As we are heavily dependent on machines that convert heat into power, their improvement in terms of efficiency and power produced has been an important topic for many years. Under these circumstances, an ERC grant was awarded to the REACHER project, with the objective of studying the effects of replacing the inert working fluids used in heat pumps and power cycles with reactive ones.[1][2]

Objectives and stakes

The main goal of this project is to develop and apply a methodology to establish the optimal architecture of different thermodynamic cycles considering a specific reactive working fluid, either to produce energy or to pump heat.

Methodology / Experimental approach

In short, the fundamental steps of this project are the following ones:



1) For a given reactive fluid and a specific application, the architecture is optimized starting from a known system (e.g. Brayton cycle).
2) The optimized couples (reactive fluid and its preferred architecture) are compared using performance indicators fitted to the considered application.
3) The better solutions are benchmarked using their counterpart inert fluids to quantify the improvement.

The calculations required to simulate the compression, expansion, heating and cooling of the fluids will be done by using FORTRAN.

Main results

Since the PhD project recently started, no significant results have been yet obtained. As preliminary work, a code has been developed to solve every point in a Brayton cycle for multiple fictive reactive fluids with the objective of validating the proposed approach with previous results obtained by the team, where it was demonstrated that reactive fluids could allow a more efficient and/or powerful operation of thermodynamic cycles by reducing the energy required during compression and increasing the work generated during the expansion of the fluid.[1]

References

[1] Lasala, Silvia & Privat, Romain & Herbinet, Olivier & Arpentinier, Philippe & Bonalumi, Davide & Jaubert, Jean-Noël. (2021). Thermo-chemical engines: Unexploited high-potential energy converters. Energy Conversion and Management. 229. 113685. 10.1016/j.enconman.2020.113685.
[2] Barakat, Aya & Lasala, Silvia & Arpentinier, Philippe & Jaubert, Jean-Noël. (2022). The original and impactful exploitation of chemical energy in heat pumps. Chemical Engineering Journal Advances. 12. 100400. 10.1016/j.ceja.2022.100400.

The thermodynamic and kinetic study of pyrolysis and combustion of organophosphorus compounds, and the provision of methods and models

By Vishal Kumar Porwal, post-doctoral researcher

Supervisors: René Fournet, Pierre-Alexandre Glaude, Baptiste Sirjean

Keywords Thermodynamics Kinetics Pyrolysis Combustion Organophosphorus compounds Modeling

CITHERE, CNRS-DGA

General context, scientific issue

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.

Objectives and stakes

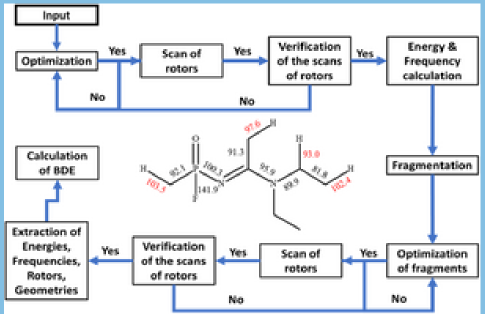
The study is divided into three parts. The first part of the study will focus on the implementation of the methodology developed previously by Lizardo-Huerta et al for three specific organophosphorus compounds.[3] The second part of the study will relate to the upgrading of the base of reactions of phosphorus-containing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

Methodology / Experimental approach

We 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. sarin, etc.) are performed using computationally cheap but reasonable methods and then the gas phase enthalpy of formation (ΔfH°298K) is calculated using the higher level theories using the methods used by Klippenstein et al.[4]

We 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 then perform the kinetic and analytical simulations at high temperatures and pressure using the Chemkin[1] package to draw the decomposition pathways of the target molecule. The same steps will be repeated for the organophosphorus molecules in the liquid medium to complete the database.



The simplified overview of the automatization script. In the middle: BDEs at 298 K of molecule A in kcal/mol, obtained using QCISD(T)/cc-PV∞(Q)Z//B2PLYP-D3/6-311+G(2d,d,p) in Gaussian16.[5]

Initial results

Keeping in mind the goal of the project which is to study the kinetics of thermal decomposition of organophosphorus compounds in the gas phase, we started with a benchmark study of smaller organophosphorus compounds using simpler ab initio theories. During benchmark studies, we developed an automatization script (see the figure) to calculate BDEs for molecule A (see the figure). This script performs geometry optimization of the whole structure at B2PLYPD3/6-311+g(2d,d,p) in Gaussian 16.[5] To make sure that we have obtained a global minimum, it performs the scan of each dihedral possible in the molecules at the B3LYP/6-311+g(2d,d,p) level. In case, it finds a local minimum, it repeats this process until obtains the global minimum. Following this, it fragments the molecule to calculate the BDE of each bond QCISD(T)/cc-PV∞(Q)Z//B2PLYP-D3/6-311+G(2d,d,p) by performing the same steps. All of these calculations are performed in the high-performance computing cluster of the Université de Lorraine also known as EXPLOR.

Using BDEs, we can eliminate some of the reaction paths, decide the initiation of the mechanism, and simplify our mechanism. Apart from the C-C fission reactions, we will also go through other initiation reactions involving the metathesis. Once the initiation reactions have been well established, the following step would be to study the propagation of the decomposition involving β-scission and H-abstraction and in the end, finalize our mechanism with the termination step. After establishing the pyrolysis of organophosphorus compounds, we will move on to the combustion and improve our mechanism.

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.

3 J.-C. Lizardo-Huerta, B. Sirjean, L. Verdier, R. Fournet and P.-A. Glaude, Proc. Combust. Inst., 2021, 38, 719–727.

4 S. J. Klippenstein, L. B. Harding and B. Ruscic, J. Phys. Chem. A, 2017, 121, 6580–6602.

5 Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, et al., Gaussian, Inc., Wallingford CT, 2016.

Analysis and development of a new carbon deposition process

By Yann Quiring, 2nd year

Supervisors: Eric Schaer, René Fournet

Keywords r-CVI Modeling Pyrocarbone C/C material

CITHERE, MBDA

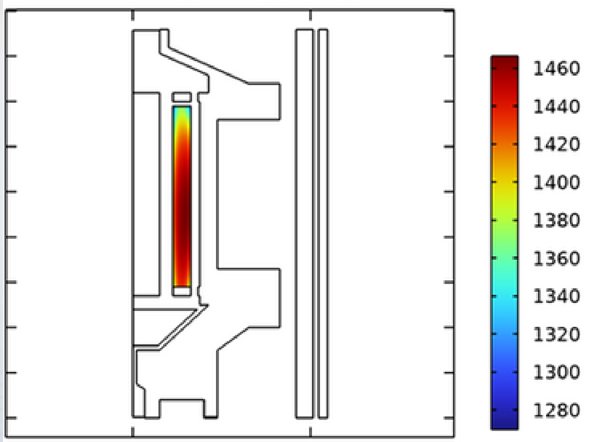
General context, scientific issue

MBDA is seeking to develop knowledge and skills on the rapid chemical vapor infiltration process (r-CVI), 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.

Methodology / Experimental approach

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

The model is 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 is 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 are simulated using conduction and convection equations. The chemistry has been adapted from the research of Rémy Lacroix and Isabelle Ziegler on the mechanisms of pyrolysis and deposition from propane. [1-2]



Density of the preform after densification (kg/m3)

Objectives and stakes

The stake of this work is to understand and improve the r-CVI process. The objectives are first to understand the chemistry, hydrodynamic 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 define optimal parameters for densification. Another goal could be to propose designs of tooling parts to improve the properties of the final material.

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.

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.

Kinetic study of a hypersonic vehicle fuel

By Boris Roux, 3rd year

Supervisors: René Fournet, Yves Simon

Keywords Jet fuel combustion Combustion mechanism Scramjet fuel Jet fuel pyrolysis Jet fuel oxidation Kinetic modelling Detailed mechanism generation

CITHERE, MBDA

General context, scientific issue

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.

Methodology / Experimental approach

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:

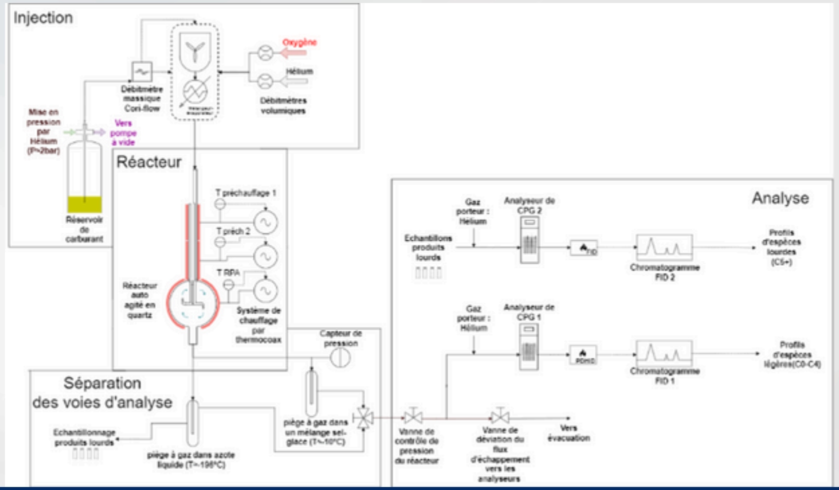
For this, an experimental pilot (see illustration) was set up to be able to make oxidation and pyrolysis between 600°C and 1000°C (depending on the studied compound), a residence time ranging from 0.5s to 4s and an equivalence ratio between 0.7 and 1.3. The products formed will be analyzed and quantified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

References

1. Andersen PC, Bruno TJ. Thermal Decomposition Kinetics of RP-1 Rocket Propellant. Ind Eng Chem Res. 1 mars 2005;44(6):1670-6.
2. Fau G, Gascoin N, Gillard P, Bouchez M, Steelant J. Fuel pyrolysis through porous media: Coke formation and coupled effect on permeability. Journal of Analytical and Applied Pyrolysis. mai 2012;95:180-8.
3. de Saint Laumer JY, Cicchetti E, Merle P, Egger J, Chaintreau A. Quantification in Gas Chromatography: Prediction of Flame Ionization Detector Response Factors from Combustion Enthalpies and Molecular Structures. Anal Chem. 1 août 2010;82(15):6457-62.
4. Frisch M, Trucks G, Schlegel H, Scuseria G, Robb M, Cheeseman J, et al. Revision D. 01, Gaussian. Inc, Wallingford CT. 2009;
5. DESIGNS ME. Chemkin-pro. 2011;



Description of the experimental setup

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.

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.

Development of a thermodynamic model and computational tools to assess the energy conversion of reactive working fluids in thermodynamic cycles

By Konstantin Samukov, 3rd year

Supervisors: Romain Privat, Silvia Lasala

Keywords Reactive fluids Thermodynamics Thermal energy conversion

CITHERE

General context, scientific issue

This thesis aims to contribute to the development of a highly efficient and extremely compact energy conversion closed cycle, whose promising - and still untapped - performance is due to the use of a reactive working fluid, instead of a conventional inert fluid. In this thesis, thermodynamic models will be developed as well as algorithms and computational codes to allow the calculation of the properties of reactive fluids, in thermodynamic cycles.

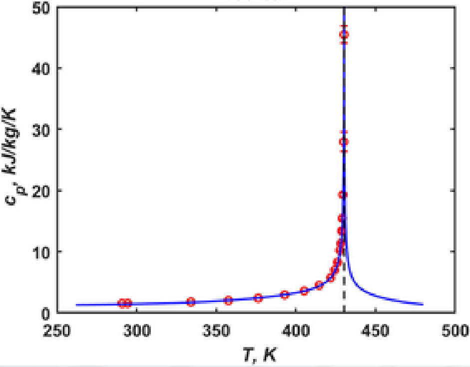
Objectives and stakes

The main objective of the thesis is to develop a computational tool for the prediction of the thermodynamic properties of inert and reactive mixtures.

Methodology / Experimental approach

Calculation tool will be entirely coded in Fortran, and will require the preliminary selection 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 perform real fluid calculations in the ERC project « REACHER » funded by Horizon Europe. In addition, it will make possible to carry out thermodynamic calculations on fictive reactions on the basis of the design and the selection of the real fluids to be characterized. 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, in the years 1960 - 1980.



Specific heat capacity at 100 bar in the reactive $N_2O_4 \rightleftarrows 2NO_2$ system: red points – experimental data, blue lines – calculations

Main results

The Peng-Robinson equation of state combined with advanced mixing rules is chosen to describe the $N_2O_4 \rightleftarrows 2NO_2$ system; the residual part of an activity coefficient model in the mixing rule was assumed to be null. The EoS input properties of pure compounds, that are the critical properties, and the acentric factors of pure N_2O_4 and NO_2 have been estimated by molecular Monte Carlo simulations. These input parameters, as well as standard molar enthalpy and entropy of the reaction $N_2O_4 \rightleftarrows 2NO_2$ at 298.15 K determined from quantum chemistry calculations, were optimized in order to reproduce best experimental data on vapor pressure and densities of liquid and vapor at vapor-liquid equilibrium. Objective function was calculated according to following procedure:

·For experimental temperatures, the system of equations describing properties of the phases, phase and chemical equilibria were solved for VLE pressure, molar volumes and molar compositions of the coexisting phases; from molar volumes and molar compositions densities of coexisting phases were evaluated [3].

·The coordinates of the unique critical point of the reacting system were calculated by a modification of an algorithm proposed for non-reactive systems [4].

·Objective function was calculated as sum of relative deviations of equilibrium vapor pressure, density of liquid and vapor at VLE, critical temperature and pressure.

Optimized parameters were used to evaluate thermodynamic properties (density, isobaric heat capacity, enthalpy, speed of sound) of the reactive system in liquid phase by implementation of RAND method [5]. This method will be used for describing different reactive mixtures: (1) involving a reacting binary fluid (i.e., the system $N_2O_4 \rightleftarrows 2NO_2$) in presence of an inert compound (CO_2); (2) involving a reacting fluid with two chemical reactions (system $N_2O_4 \rightleftarrows 2NO_2 \rightleftarrows 2NO + O_2$).

References

[1] S. Lasala, R. Privat, O. Herbinet, P. Arpentinier, D. Bonalumi, and J.-N. Jaubert. Energy Convers. Manag. 2021: 113685.
[2] Website of the project REACHER: https://www.univ-lorraine.fr/erc-reacher/
[3] S. Lasala, K. Samukov, H. M. Polat, V. Lachet, O. Herbinet, R. Privat, J.-N. Jaubert, O. Moultos, K. de Ras, T. J. H. Vlugt. Chem. Eng. J. 2024, 483: 148961.
[4] M. Cismondi, M. L. Michelsen. J. of Supercritical Fluids 2007, 39: 287-295.
[5] C. Tsanas, E. H. Stenby, W. Yan. Ind. Eng. Chem. Res. 2017, 56 (41): 11983-11995.

Ozone-Initiated Oxidation of Fuels in a Jet-Stirred Reactor

By Caroline Smith Lewin, 3rd year

Supervisors: Frédérique Battin-Leclerc, Jérémy Bourgalais

Keywords Ozone-initiated oxidation | Jet-stirred reactor | FTIR | NOx analyzer

CITHERE

General context, scientific issue

Ozone (O3) addition is one of the promising methods to achieve improvement and control of combustion/ignition processes. However, the complex chemistry induced by O3 reaction makes investigations on O3-assisted oxidation at combustion-relevant conditions still scarce.

Methodology / Experimental approach

O3-initiated oxidation of NH3 was studied in a jet-stirred reactor (JSR) operating at near-atmospheric pressure and temperatures from 700 to 1200 K. Mole fractions profiles were measured using a Fourier transform infrared (FTIR) spectrometer and a chemiluminescence NOx analyzer and compared to the predictions of a kinetic model [3] updated with an O3-submechanism [4].

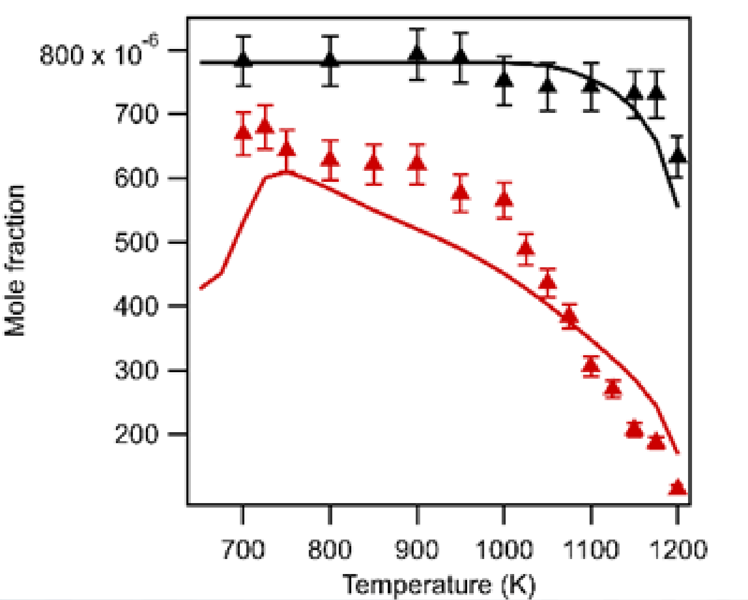


Fig. NH3 profile (black and red data correspond to O3-free and O3-addition cases, respectively)

Objectives and stakes

The focus of this year was to study O3-initiated oxidation of ammonia (NH3), an attractive carbon-free fuel option despite the practical challenges associated with its application [1]. O3 has the potential to enhance NH3 ignition through its thermal decomposition into O-atom and O2 [2].

Main results

NH3, NO, NO2, N2O and H2O mole fractions were measured as a function of temperature. The addition of O3 allowed NH3 reactivity from 700 K and full consumption at 1200 K, in contrast to a start of reactivity above 1100 K for the case without O3 (see Fig.). Relatively good agreement between experiments and simulations was found for NH3 mole fraction, whereas improvements are needed to predict correctly produced species.

References

[1] Herbinet O. et al., Fuel Comm. 2022, 100064.
[2] Sun W. et al., Prog. Energy Combust. Sci. 2019, 73:1–25.
[3] Stagni A. et al., Chem. Eng. J. 2023, 471:144577.
[4] He X. et al., J. Phys. Chem. A 2023, 127:1923–1940.

Impacts of multifunctional environments on the liquid phase oxidation of biosourced technical fluids

By Yireth Andrea Vega Bustos, 1st year

Supervisors: Mickael MATRAT, Baptiste SIRJEAN, Isabelle HENAUT

Keywords Oxidation Technical fluids Renewable fluids Shear Electromagnetic field

CITHERE

General context, scientific issue

The new technologies developed for decarbonizing our industry and transports have changed technical fluids integration and specifications. Moreover, the decarbonization policy has directed fluids formulation towards bio-sourced or synthetic products. However, the impact of different constraints on their performance must be assessed to satisfy the sustainability and performance needs.

Methodology / Experimental approach

This work consists of 3 parts: definition of fluids matrix, characterization of constraint's impact on liquids phase oxidation process and finally modeling of the impact structure-properties.

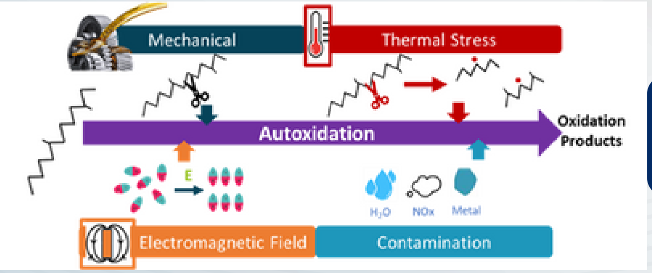
1. Definition of fluids matrix: It was built from fluids that have similar properties compared to relevant options identified on the market.
2. Characterization of the impact of constraints on liquid phase oxidation process of fluids

The bibliographic research has shown that some constrains have an effect on fluid oxidation, but these studies remain qualitative. To rigorously evaluate the oxidation response in these types of environments, the following approach is proposed:

a rheometer will be used to apply constraints (mechanical stress, thermal stress, electromagnetic field) to the oil, but with limited amplitudes. Next, the oxidation will be tested in an accelerated oxidation test (RapidOxy 100) at temperatures ranging between 120°C – 160°C, followed by iodometric titration and other characterization methods. Then, the constraints will also be applied in a microfluidic reactor (in development) where constraints will be amplified and property tracking improved.

3. Modeling of the impact structure-properties

According to the obtained results, the use of existing models will be explored to identify their potential for processing the new database. Models include approaches like chemometrics or QSPR modeling (quantitative structure property relationship).



Effect of each constraint on the liquid phase oxidation process according to literature.

Objectives and stakes

The objective of this thesis is to investigate the impact of multifunctional environments (involving interplay of constraints) on fluids oxidation. Several secondary objectives were set:

1. Establish the experimental methods to study the oxidation process under multiple constraints
2. Assess quantitively and qualitatively the impact of physical and chemical constraints on the liquid phase oxidation process.
3. Evaluate the potential of machine learning modeling approaches based on structure/property relationships to correlate fluid chemistry with the effects observed during aging.

Main results

The impact of some constraints found on multifunctional environment had been studied, unfortunately only a qualitative assessment on the oxidation process is provided in the literature. Krupka et al, has demonstrated that mechanical stress induces the scission of chains, leading to an irreversible loss of viscosity [1]. At the same time, thermal stress without oxygen leads to the same effect (structure change), which can lead to a different oxidation process. Concerning contaminants such as water, metals (ex. from mechanical parts erosion) or combustion products (NOx and particles). Sarin et al. found that the presence of metals such as copper, iron, nickel, manganese and cobalt decreases the induction period of palm methyl ester, which in other studies has already shown high oxidation stability. This may be because metals act as catalysts and accelerate free radical formation [2]. Regarding the electromagnetic field literature, it is still limited. Some studies confirmed its effect on decreasing the stability of transformer oils [3]. In addition, other studies also probed its effect on tribological performance of lubricating oils, where the anti-wear and anti-friction properties were increased or decreased depending on oil's composition. Finally, Kipriyanov and Purtov demonstrated that even a magnetic field of small intensity can induce a change in the oxidation reaction mechanism [4].

However, there are many unknowns regarding the quantitative effect of each constraint and their combinations (complex environments) on the oil's oxidation process. That is why, with this thesis subject, it is expected to ultimately be able to quantify the impact, for example, of the intensity of the electromagnetic field or the presence of contaminants on the oxidation processes, as well as confirm if there is a synergistic effect between all the constraints to reduce oil's stability.

References

[1] I. Krupka, et al., Contact. Tribol Lett, 2011, 41, 191–197.
[2] A. Sarin, et al., Energy Fuels 2010, 24 (4),2652-2656.
[3] T.-O. Cujba, 9th International Conference on Environment and Electrical Engineering, 2009, 525–528
[4] Kipriyanov Jr, A. A., & Purtov, P. A. The Journal of Chemical Physics, 2011, 134(4), 044518

PRODUCT ENGINEERING

Foaming properties of aqueous solutions of natural plant proteins in relation with their interfacial rheological properties at the air/water interface

By Mohmmad Mahdi ASSAF, 2nd year

Supervisors: Thibault Roques Carmes,Tayssir Hamieh, Veronique Sadtler, Philippe Marchal, Romain Kapel, Sophie Beaubier

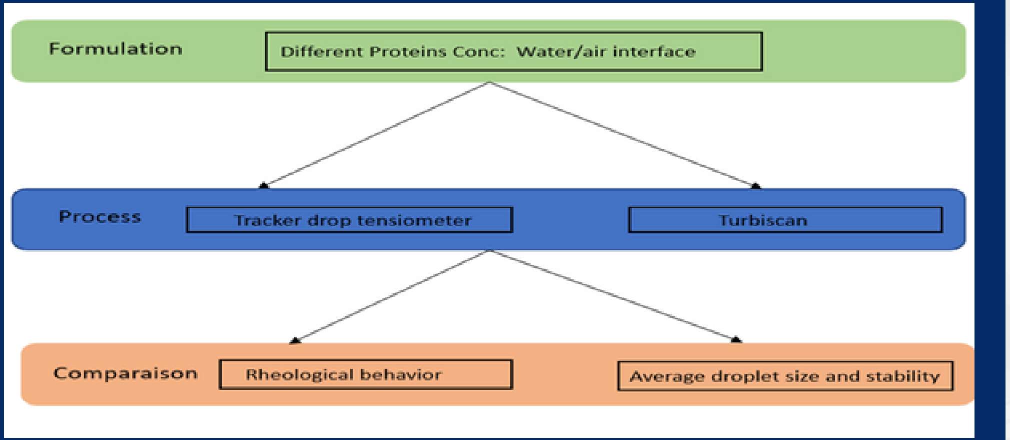
Keywords Foam | Plant proteins dilatational viscoelasticity | Drop tensiometer | Interfacial rheology | Bulk rheology | L/G interfaces

PRODUCT ENGINEERING

General context, scientific issue

Foamed foods have been a significant part of human nutrition. They are involved in a variety of formats, such as beer, ice cream, and cakes.
Liquid foams are thermodynamically unstable. To stabilize the foam, surface-active molecules are needed. Usually low molecular weight surfactants, amphiphilic polymers, and colloidal particles are used. However, to meet the demands for a circular economy, such as using molecules from renewable plant resource is essential to replace the conventional foaming agents with bio-based surface-active molecules of plant origin [1].

Methodology / Experimental approach



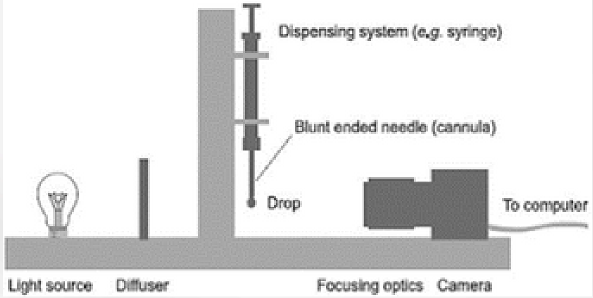
Formulation — Different Proteins Conc: Water/air interface

Process — Tracker drop tensiometer | Turbiscan

Comparaison — Rheological behavior | Average droplet size and stability

Objectives and stakes

- Study and compare the interface rheology properties of 3 plant proteins at L/G interfaces using drop tensiometer.
- investigate the link between the results obtained in bulk and interface.
- Probe the impact of the interfacial rheology properties on the foam stability.



Scheme of the experimental set-up of dilational interfacial rheology at water/air interface and turbiscan

Main results

In our search we expect to obtain relations between results of the interfacial rheological study of water/air stabilized by plant proteins molecules performed by tracker drop tensiometer (dilational rheology) and foam properties performed by Turbiscan. This work will provide many information about the influences of interfacial rheology of these system on foam characterization and stability.

References

[1] 1] Luca Amagliani, Juliana V.C. Silva, Maxime Saffon, Jannika Dombrowski. Trends in Food Science & Technology Volume 118, Part A, December 2021, Pages 261-272.
[2] Ce Wanga, Xu-Long Cao, Lan-Lei Guo, Effect of molecular structure of catanionic surfactant mixtures on their interfacial properties. Colloids and Surfaces A: Physicochem. Eng. Aspects 509 (2016) 601–612.
[3] Qin Jiang a, Luo-Peng Xu Li-Li Wang Jia-Zheng Wang a Lei Zhang, Lu Zhang, Dilational rheological properties of 2, 5-dialkyl benzene sulfonates at air-water and decane-water interfaces. Colloids and Surfaces A: Physicochemical and Engineering Aspects 653 (2022) 130035.

NH2-MIL-125(Ti) derived N-doped TiO2 combined with reduced graphene oxide for photocatalytic applications

By Askar Bakhadur, post-doctoral researcher

Supervisors: Raphaël Schneider

Keywords NH2-MIL-125 MOF N-TiO2 Photocatalyst rGO Visible light Photodegradation

PRODUCT ENGINEERING

General context, scientific issue

Purification of contaminated water using photocatalysts is currently a hot topic as it is a highly effective, green and cost-effective method [1]. Among photocatalysts, titanium dioxide TiO2 is the most popular due to its suitable physicochemical properties such as stability, weak toxicity and high photoactivity. However, this semiconductor can only be activated under UV light irradiation, which restricts its potential applications. Doping is one of the method allowing TiO2 to be photocatalytically active in the visible range [2]. N-doped TiO2 exhibits broad absorption in the visible region, which can allow the utilization of a large part of the solar spectrum.

Methodology / Experimental approach

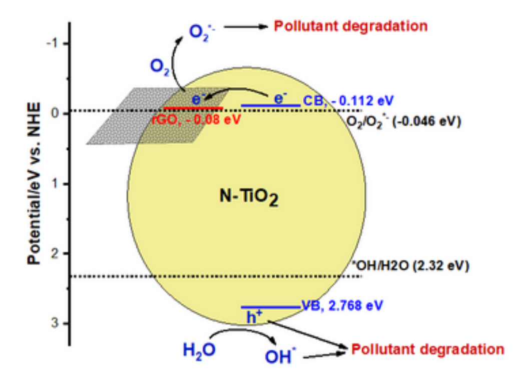
The methodology is as follows:

-Synthesis of the NH2-MIL-125(Ti) MOF by a solvothermal method. For this purpose, 2-aminoterephthalic acid and titanium isopropoxide were used as precursors.

-Investigate the effect of adding rGO on photocatalytic properties. Search for the optimal ratio of NH2-MIL-125(Ti)/rGO to obtain highly efficient heterostructured photocatalysts.

-Investigate the influence of experimental parameters (heating rate, temperature …) during the conversion of NH2-MIL-125(Ti) into N-doped on the photocatalytic properties.

-Characterization of the obtained photocatalysts and study the mechanism of the photocatalytic reaction.



Schematic illustration of the band-energy levels of N-TiO2/rGO photocatalyst

Objectives and stakes

The main objective of this work is to prepare novel MOF-derived N-TiO2-based photocatalysts combined with reduced graphene oxide (rGO) to improve the photocatalytic properties in the visible light range. Due to its high electrical conductivity, surface chemistry, dispersibility, and semiconductor properties, rGO should not only allow to decrease the charge carrier recombination but also increase the visible light absorption.

Main results

NH2-MIL-125(Ti) was successfully synthesized by a solvothermal method and subsequently annealed at 450°C for 2 h into N-TiO2 with pure anatase structure as indicated by XRD. The XPS analysis confirms that the N-doped TiO2 structure was produced. N-TiO2- x wt% rGO with different amounts of rGO was also synthesized by thermolysis of NH2-MIL-125(Ti) – GO mixture. The association of N-TiO2 with rGO leads to a significant increase in the photocatalytic efficiency. The best photocatalyst allows a complete degradation of the Orange II dye within 240 min under visible light irradiation.

Investigation of the main active species involved in the photocatalytic degradation shows that •OH and O2•- radicals, holes (h+), and singlet oxygen 1O2 play a key role.

References

1)Carvalho, I. T., & Santos, L. (2016). Antibiotics in the aquatic environments: a review of the European scenario. Environment International, 94, 736-757.

2)Gao, P., Li, A., Sun, D. D., & Ng, W. J. (2014). Effects of various TiO2 nanostructures and graphene oxide on photocatalytic activity of TiO2. Journal of Hazardous Materials, 279, 96-104.

Understanding the catalytic and chemical phenomena behind the oxidative precipitation process for the recovery of metals of interest from NMC batteries

By Roberto Barbano (1st year, PhD student)
Supervisors: Emmanuel Billy, Gaëlla Frajer, Hervé Muhr

Keywords Battery recycling Precipitation Oxidation Radicals Transition metals

PRODUCT ENGINEERING, CEA LITEN
DTNM-STDC-LVME GRENOBLE

General context, scientific issue

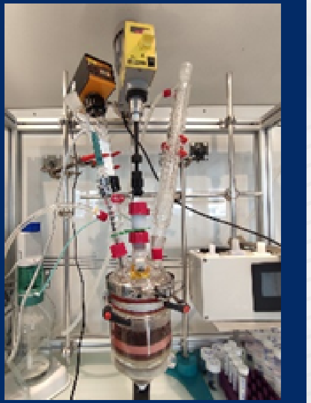
The interest and diffusion of BEVs (Battery Electric Vehicles), in Europe and the other continents, has a crucial importance for the energetic transition. Indeed, Li-ion batteries are the key technology to drive the transition, and, a closed loop recycling economy would enhance the EU's strategic autonomy in terms of supply chain of critical materials. Global demand of Li-ion batteries is expected to drastically raise from about 700 GWh in 2022 to around 4.7 TWh by 2030 and, the batteries used for mobility applications will account the major share of the market [1]. Hence, the need for efficient and economically sustainable recycling processes, such as the oxidative precipitation[2], to recover the metals of interest used for the synthesis of the active materials present on the electrodes.

Objectives and stakes

Objective is to understand the interactions between the oxidant species and the cobalt ions that can activate it, to look for correlations between the operating conditions and the selectivity of the process. It is assumed that the morphology of the precipitate may also play a key role on the selectivity of the Mn precipitation process, as Co adsorption and co-precipitation phenomena may occur in the porous structure of the Mn precipitate. The role of morphology is to be correlated and explained with the reaction mechanism and how this is influenced by the operating conditions

Methodology / Experimental approach

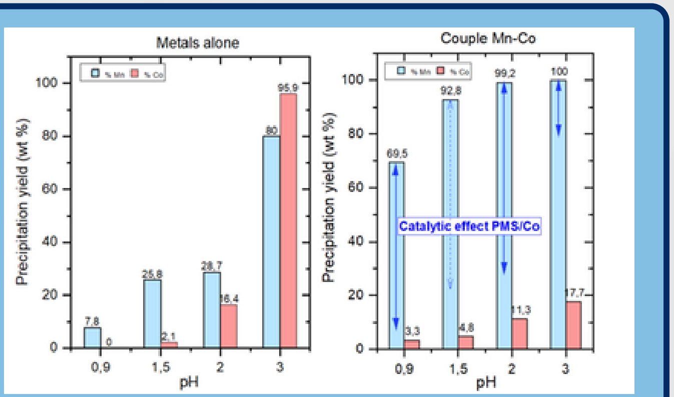
Experiments of oxidation-precipitation are conducted with 1 l double-jacket reactor and a titration system is used to control the pH with a solution of 1 M of NaOH. Synthetic solutions of Co, Mn and Ni are used for precipitation tests to have a high reliability of the results. ICP measurements are conducted to analyze the concentration of metals in the reactive solution. After the precipitation test, the solid is recovered by filtration, washing, drying for one night at 90 °C. MEB observation and laser granulometry are used to characterise the solid.



Experimental set-up : reactor used for the oxidative-precipitation test

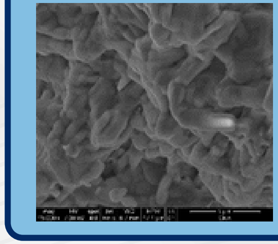
Main results

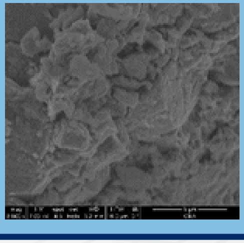
First precipitation tests showed that the precipitation efficiency of Co and Mn alone in solutions increases with pH, which is in line with the thermodynamics and the evolution of the potentials of the oxidation reactions and the PMS couple (oxidazing species used).

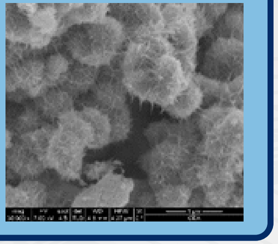


Second sequence of precipitation test was conducted in the same conditions and the Mn and Co together in the same solution. It is possible to see a clear increase of the precipitation yield of Mn for all the pH conditions, instead, the Co precipitation is decreased, because it is reacting preferentially with PMS and Mn instead of precipitating.

Subsequently, the morphology of the precipitate was analysed, in particular, when Mn and Co precipitate alone, they form a very compact structure. In contrast, when they precipitate together, a more porous structure of the Mn precipitate and a surface area conducive to adsorption phenomena can be observed.







References

[1] "www.mckinsey.com." [Online]. Available: www.mckinsey.com
[2] E. Billy, S. Barthelemy, Procede de recyclage des batteries Li-ion, Commissariat a l'energie atomique et aux energies alternatives, France, FR3102008A1, 2019,

Development of an ultrafiltration process for the purification of sunflower albumins

By Paula Barrera-Ariza, Research Engineer

Supervisors: Romain Kapel, Sara Albe-Slabi

Keywords Plant protein Sunflower albumin Ultrafiltration Purification

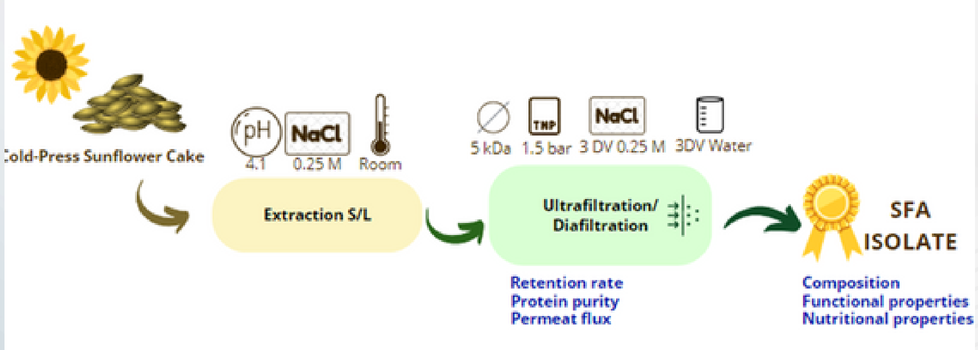
PRODUCT ENGINEERING

General context, scientific issue

The rising demand for proteins drives the development of new plant-based protein ingredients for food industry. Sunflower albumins (SFA) having good nutritional and functional properties are promising alternative. However, a suitable process for their extraction and purification is required.

Methodology / Experimental approach

To develop the process for production of SFA two stages were carried out: first, the optimal extraction conditions for selective SFA were selected using response surface methodology and multicriteria optimization. Secondly, the membrane separation process was explored for purification of extracted SFA. To do so, membrane parameters such as cut-off and TMP were established considering the process performance such as retention rate of SFA, total proteins, chlorogenic acid, phytic acid, and sugar as well as the productivity in terms of flux. Then, appropriate scenario of diafiltration (diafiltration solvent, ionic strength, diavolumes number) was searched. Finally, the composition, the structural and functional properties of produced SFA isolate were determined.



Process flow diagram to produce sunflower albumin isolate

Objectives and stakes

The objective of this project was to establish the suitable conditions for production of SFA isolate from sunflower cold-press meal. The main criteria were the process yield, isolate composition, efficiency in the elimination of antinutritional compounds (phytic acid, phenolic compounds, sugars) and quality of SFA in terms of nutritional, functional and structural properties.

Main results

Multicriteria optimization of extraction process allowed to select pH 4.1 and 0,25 M NaCl as the optimal conditions for SFA isolation from cold-press meal. These process conditions yielded extraction yield of SFA superior to 75% and the excellent selectivity of SFA representing 90% of total proteins.

Regarding membrane parameters, our study showed that a plane membrane with a cut-off of 5 kDa with a transmembrane pressure (TMP) of 1.5 bar was efficient to retain the majority of SFA, while removing the antinational compounds. The final retention of SFA was 96.94%±0.36 and the permeate flow was 15.40±1.39 L/h/m2 for the 3 DV with 0,25 M NaCl, followed by 3.30±0.52 L/h/m2 for the 3 DV with water. The SFA produced at a pilot laboratory scale had an isolate grade (89.9% of proteins) and was low in chlorogenic acid (3.3%), phytic acid (2.9%), and carbohydrates (3.3%). The isolate was also well-soluble in water (from 88.2%±1.5 to 91.7%±1.0 in a pH range of 3 to 9) and had good emulsifying properties (capacity 31.2%±4.7 and stability of 85.0%±7.1).

References

[1] Albe-Slabi, S., Mathé, C., Basselin, M., Fournier, F., Aymes, A., Bianeis, M., Galet, O., & Kapel, R. (2020). Optimization of sunflower albumin extraction from oleaginous meal and characterization of their structure and properties. Food Hydrocolloids, 99, 105335. https://doi.org/10.1016/j.foodhyd.2019.105335

[2] Albe-Slabi, S., Mathe, C., Basselin, M., Framboisier, X., Ndiaye, M., Galet, O., & Kapel, R. (2020). Multi-objective optimization of solid/liquid extraction of total sunflower proteins from cold press meal. Food Chemistry, 317, 126423. https://doi.org/10.1016/j.foodchem.2020.126423

[3] Pickardt, C., Eisner, P., Kammerer, D. R., & Carle, R. (2015). Pilot plant preparation of light-coloured protein isolates from de-oiled sunflower (Helianthus annuus L.) press cake by mild-acidic protein extraction and polyphenol adsorption. Food Hydrocolloids, 44, 208–219. https://doi.org/10.1016/j.foodhyd.2014.09.020

Hydrodynamic instabilities of a shear thinning fluid in a rotative filtration process

By Sara Ben Sadek (First year Ph.D. student)
Supervisors: Cécile Lemaître, Chérif Nouar

Keywords Rotative filtration · Non-Newtonian fluid · Hydrodynamic instabilities · Taylor Couette flow

PRODUCT ENGINEERING, LEMTA

General context, scientific issue

Rotative filtration process plays a major role in a variety of purposes due to its versatility, its performances and the range of membrane type and pore sizes available. One of the most relevant applications is the reuse and recycling of water, which is a necessity for the growing global water stress.

Objectives and stakes

Filtration processes are limited by the problem of fouling due to particle accumulation on the filter wall. Rotative filtration limits this issue through secondary flows, which resuspend accumulated particles. It consists of a vertical rotating porous cylinder placed in a coaxial cylindrical tank. The objectives of this PhD is to model and optimize this process, and in particular to understand the interplay between hydrodynamic instabilities, particle transport and the rheology of a suspension.

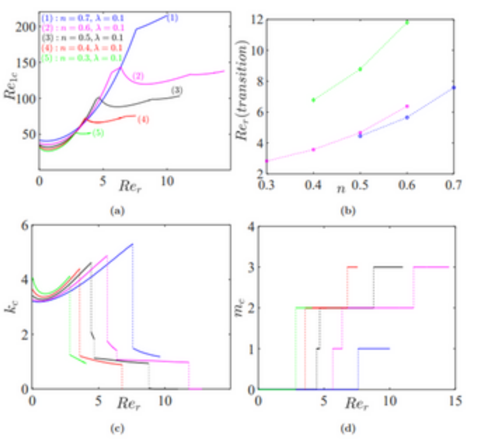
Methodology / Experimental approach

Due to the complexity of the flow in rotative filters (Taylor-Couette flow combined with axial and radial flows), which involves a large number of parameters, we will consider systems of growing complexity. We will first consider Taylor-Couette flow with a radial flux (radial Reynolds number). Then, an axial flow will be superimposed (dimensionless pressure gradient). The suspension will be assumed to be shear-thinning described by a Carreau model (parameters and).

The flow is governed by the mass and momentum conservation equations. The base state is calculated with an iterative method. Then, an infinitesimal perturbation is superimposed to the base flow. The perturbations equations are then linearized and decomposed into Fourier modes. The resulting eigenvalue problem is discretized using a spectral collocation method based on Chebyshev polynomials evaluated at N collocation points of Gauss-Lobatto and solved using QZ algorithm with Matlab. Marginal stability conditions are determined for a given azimuthal wavenumber m and different values of the axial wavenumber k. The minimum rotational Reynolds number, , for which the real part of one eigenvalue is positive, corresponding to the appearance of the 1st instability is reported.

Main results

The shear-thinning character introduces a modification of the base state, in particular the wall shear-rate which plays a role in the transfer of energy from the basic flow to the disturbance. Furthermore, a nonlinear variation of the viscosity with the shear-rate gives rise to an anisotropy in the viscous dissipation. For Newtonian fluids, without an axial flow, recent studies have shown the emergence of a new oscillatory mode, characterized by very low or even zero axial wavenumbers , it takes the form of a wave propagating in the azimuthal direction [3,4]. The influence of the non-Newtonian character and that of the axial flow on this oscillatory mode, has been investigated. It appears that the shear-thinning character destabilizes the flow: the first instability occurs for lower critical rotational Reynolds numbers. Furthermore, it facilitates the appearance of the oscillatory mode, at lower radial Reynolds numbers than for Newtonian fluids.



Influence of shear-thinning effects on the variation of the critical Reynolds number (a), axial (c) and azimuthal (d) wave numbers as a function of the radial Reynolds number. Case of a wide gap η = 0.4. (1) n = 0.7, (2) n = 0.6, (3) n = 0.5, (4) n = 0.4 and (5) n = 0.3. The constant time of the fluid is fixed λ = 0.1. Subfigure (b) gives the radial Reynolds number at which the transition to an oscillatory mode, with m = 1, m = 2 and m = 3 is observed as a function of the shear-thinning index.

References

[1] M.R. Ladisch and K.L. Kohlmann. Recombinant human insulin. Biotechnol. Prog, 8(6):469– 478, 1992.

[2] E. C. Johnson and R.M. Lueptow. Hydrodynamic stability of flow between rotating porous cylinders with radial and axial flow. Phys. Fluids, 9(12):3687–3696, 1997.

[3] K. Ilin and A. Morgulis. On the stability of the Couette–Taylor flow between rotating porous cylinders with radial flow. Eu. J. Mech. B Fluids, 80:174–186, 2020.

Modeling and development of an innovative medical device to test anti-cancer drugs

By Cyprien Berthelemy, 2nd year

Supervisors: Halima Alem Marchand, Cécile Lemaître, Rainier Hriez

Keywords Modeling Microfluidics Organ-on-a-chip Cancer therapy Medical Devices

PRODUCT ENGINEERING, IJL

General context, scientific issue

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].

Methodology / Experimental approach

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.

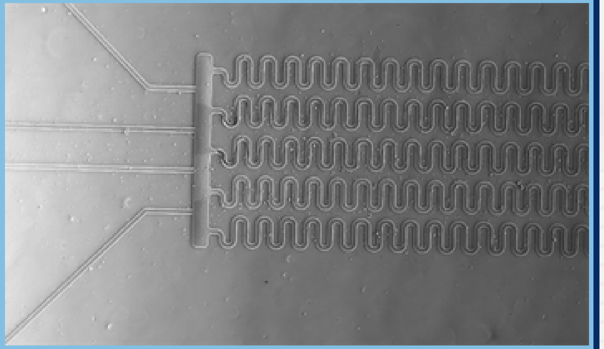


Fig. 1- Prototype of the microfluidic system perfused with colorant. A concentration gradient is apparent.

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. Most of the second year was used in order to perform this. But a lot of experimental problems (mostly clogging) hindered the obtention of reproducible results.

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.

References

[1] Venditto, V. J.; Szoka, F. C. Cancer Nanomedicines: So Many Papers and so Few Drugs! Adv. Drug Deliv. Rev. 2013, 65 (1), 80–88. https://doi.org/10.1016/j.addr.2012.09.038.

[2] Shi, J.; Kantoff, P. W.; Wooster, R.; Farokhzad, O. C. Cancer Nanomedicine: Progress, Challenges and Opportunities. Nat. Rev. Cancer 2017, 17 (1), 20–37. https://doi.org/10.1038/nrc.2016.108.

[3] Huh D, Matthews BD, Mammoto A, Montoya-Zavala M, Yuan Hsin H, Ingber DE. Reconstituting Organ-Level Lung Functions on a Chip. Science. 2010;328(5986):1662-1668. doi:10.1126/science.1188302

Green process for valorization of bioplastics: enzymatic transesterification of polylactic acid

By Alaric Catard, 3rd year

Supervisors: Sandrine Hoppe, Isabelle Chevalot

Keywords

Polylactic acid
Enzymes
Green solvents
Hydrolysis
Novozym 435®
PLAase III
Transesterification

PRODUCT ENGINEERING

General context, scientific issue

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 lack of recycling industries for it requires the development of recycling processes.

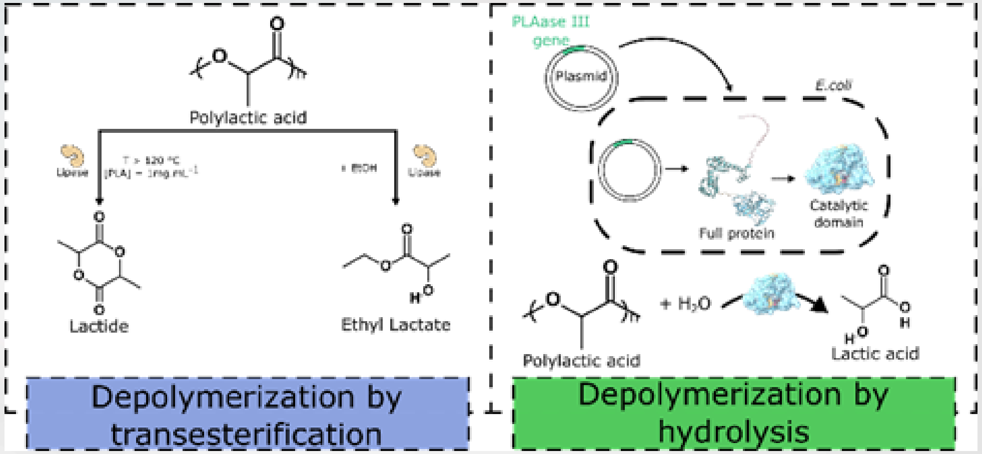
Objectives and stakes

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 (Novozym 435®) using sustainable solvents to catalyze transesterification reaction. 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 / Experimental approach

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 different green solvents, (2) the residual activity of the enzyme after different times at high temperatures in these solvents. After that, the enzymatic cyclo-depolymerization and transesterification with ethanol have been carried out and the molecular sizes of the products have been analyzed using size exclusion chromatography and their structural composition by 1H NMR.

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. The presence and identification of the catalytic domain 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.



Schematic representation of the different depolymerization pathways explored in this PhD

Main results

It has been shown that PLA is soluble at 100°C in diethyl carbonate (DEC) and anisole: 120 g.L-1 Moreover, the immobilized enzyme keeps a significant activity at 120°C in anisole rather than DEC: 78.4% and 0% in anisole and DEC respectively after 48h. Depolymerization reactions of PLA by enzymatic transesterification (i.e. cyclo-depolymerization and alcoholysis) have led to preliminary results: enzymatic cyclo-depolymerization is dependent on initial molecular weight of PLA but very limited and alcoholysis enabled the formation of ethyl lactate, usable as a green solvent.

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 complete enzyme (pro and catalytic regions) in small volumes has been achieved. Esterase and protease activity tests showed low activities for certain plasmids, E.coli strains and culture conditions. However, a large quantity of PLAase is produced in the form of inclusion bodies, making it insoluble. Enzyme engineering approaches are in progress to overcome this issue and to get a more thermostable and active enzyme than wild-type PLAase.

Photoluminescent textiles incorporating QDs/photopolymer composites: towards a new generation of lighting devices

By Bilel CHOUCHENE (research engineer)

Supervisors: Raphaël SCHNEIDER

Keywords Quantum dots (QDs), CuInS2/ZnS AgInS2/ZnS Photoluminescence QDs/photopolymer composites Lighting devices

PRODUCT ENGINEERING

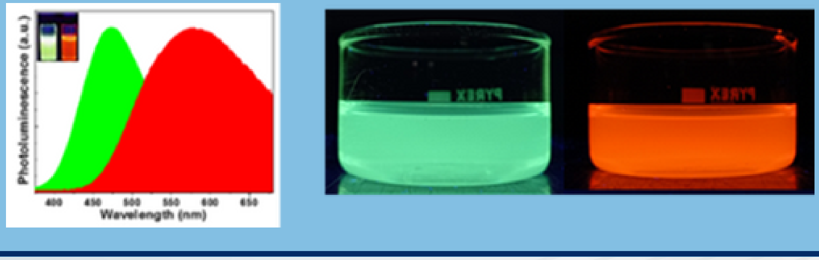
General context, scientific issue

Luminescent nanoparticles (NPs) have been extensively utilized in various research and application fields, particularly in the realm of light-emitting diodes (LEDs) [1,2]. Within this context, our work focuses on developing a new generation of NPs with exceptional properties for advanced applications in LED technology.

Methodology / Experimental approach

To achieve the aforementioned objective, the following methodology will be implemented:

1. Synthesis of silver- or copper-based QDs with tunable optical properties in the visible range.
2. Structural and optical characterization of the synthesized QDs, along with an assessment of their photostability.
3. Development of a photo-induced synthesis process for highly photoluminescent QDs/polymer nanoassemblies. This involves adjusting the size, composition, and spatial distribution of QDs within the polymer film, and applying this technology to textile applications.
4. Preparation of new photoluminescent textiles with targeted photometric characteristics, optimized for use with violet/blue LED chips.
5. Demonstration of the process feasibility by producing 10 linear meters of functionalized textile on a semi-industrial scale.



PL emission spectra of green and red QDs (at left) and Digital photographs of the prepared QDs solubilized in solutions. (at right)

Objectives and stakes

The primary objective of this work is to create innovative photoluminescent textiles by coating them with an advanced composite film. This film integrates heavy metal-free, non-toxic quantum dots (QDs) with a biocompatible light-cured methacrylate formulation, paving the way for a new generation of photoluminescent textiles.

Main results

Red, orange, yellow, and green-emitting CuInS2/ZnS, AgInS2/ZnS, and AgCuInS2/ZnS quantum dots (QDs) were synthesized using a thermal decomposition method from precursors in either organic or aqueous phases. Analysis of the crystal structure and phase of the prepared QDs was conducted via X-ray powder diffraction (XRD), revealing their crystallization in the tetragonal chalcopyrite phase (JCPDS 40-1488) [3]. Transmission electron microscopy (TEM) analysis indicated spherical-shaped particles with an average size on the order of 2.5 nm.

These synthesized particles exhibit high photoluminescent properties, with quantum yields ranging from 40% to 80%. Photostability tests demonstrated their resilience under UV irradiation at 405 or 450 nm.

The prepared QDs displayed low stability in solution when using methacrylate monomers or in toluene. To overcome this challenge, the polymerization of these QDs into films using polyvinyl polymers was conducted. This process significantly improved the photostability of the prepared QDs under LED irradiation at 405 or 450 nm.

References

[1] Yasuhiro Shirasaki, Geofrey J. Supran, Moungi G. Bawendi and Vladimir Bulović, Nature Photonics 7, 2013, 13-23.

[2] Hee Chang Yoon, Ji Hye Oh, Minji Ko, Heeyeon Yoo, and Young Rag Do, ACS Appl. Mater. Interfaces 7, 2015, 7342–7350.

[3] Zhe Hu, Hanxu Lu, Wenjie Zhou, Jinxin Wei, Hanqing Dai, Hong Liu, Zhiyong Xiong, Fengxian Xie, Wanlu Zhang, Ruiqian Guo, J. Mater. Sci. Technol. 134 (2023) 189.

Valorisation of proteinic meal effluent produced from oilseeds by lactic acid bacteria

By Christophe Derrien, 2nd year
Supervisors: Annie Dary-Mourot, Romain Kapel

Keywords Agro-resources valorisation | Phytase | Lactic acid bacteria | Phytic acid | Process engineering

PRODUCT ENGINEERING, CALBINOTOX

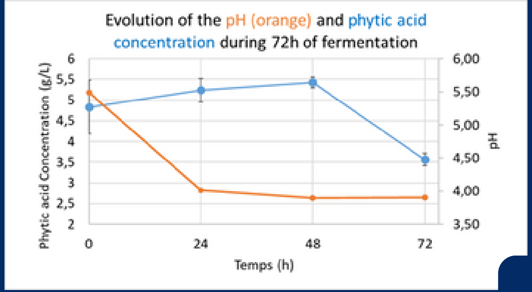
General context, scientific issue

Oilseed meals are rich protein sources obtained from the oil industry (1). Production of proteinic ingredient from oilseeds such as concentrate and isolate generates liquid effluents that contains carbohydrates, phenolic compounds, phytic acid and a large fraction of protein including albumins. Purifying albumins to manufacture protein isolate for the food industry is a promising way of valorization for these effluents. However, phytic acid, an antinutritional factor (ANF), can complex to albumins (2) which diminishes protein digestibility (3). Phytic acid elimination is therefore necessary to obtain bioavailable protein.

Methodology / Experimental approach

First, lactic acid bacteria were screened for phytase activity with the use of phytase screening medium (PSM). Then the production of phytase was studied by following phytase activity simultaneously to bacterial growth. Simultaneously, candidate genes of phytase were selected from a LAB and amplified for heterologous expression. Besides, effluent was produced from sunflower meal in acidic condition and the effect of de-phytinisation on albumin purification by diafiltration was studied. The amount of phytic acid and albumins were measured during this process.

Finally, the conditions of separation between the cells and the fermented effluent will be assessed and different membrane processes will be study for albumin purification. LAB behavior, alone or in co-culture will be evaluated with kinetics studies to determine the best conditions in which phytase is expressed as well as the capacity to hydrolyze phytic acid.



Evolution of the pH and phytic acid concentration during fermentation by lactic acid bacteria

Objectives and stakes

Phytase can be used to unbound protein from phytic acid, however they present several downsides. They are expensive enzymes; are pH and temperature dependent; are also sensitive to high temperature. Lactic acid bacteria (LAB), that are commonly used in the food industry, have been identified as phytase producer (4). Proteinic effluents contains molecules such as sugars and non-proteinic nitrogen, that are suitable with development of such bacteria. The objective of this work is then to evaluate the elimination of phytic acid from this medium by phytase treatment and through fermentation of effluents by LAB in order to facilitate albumin's valorization.

Main results

One strain of lactic acid bacteria has been identified as phytase producer and the expression of phytase during bacterial growth was observed. Candidate genes were selected and heterologous expression in E. coli BL21 has been correctly performed. Induction of the protein of interest has been done and an IMAC method was optimized for purification. As of this day, no activity has been detected on purified product. This observation could result from different factors such as an error in the selection of the genes or the purified protein is in a misfolded conformation and therefore lost its activity.

First batches of oleaginous meal extraction were done and study of bacterial growth in such medium as started. Preliminary studies indicate that the selected strain has the capacity to grow in effluent and a reduction of around 25% was observed in 72 hours. More data are needed to confirm the observed trend. The effect of phytate removal in sunflower effluent was also studied and results showed that phytase treatment allowed better recovery of albumins. More analysis is required to characterize the proteins and their techno-functional properties (Foaming, Emulsifying).

References

1. Arrutia F, Binner E, Williams P, Waldron KW. Oilseeds beyond oil: Press cakes and meals supplying global protein requirements. Trends in Food Science & Technology. 1 juin 2020;100:88-102.
2. Kumar V, Sinha A, Kajbaf K. Phytic Acid and Phytase Enzyme. In 2019. p. 467-84.
3. Selle PH, Cowieson AJ, Cowieson NP, Ravindran V. Protein–phytate interactions in pig and poultry nutrition: a reappraisal. Nutr Res Rev. juin 2012;25(1):1-17.
4. Sharma N, Angural S, Rana M, Puri N, Kondepudi KK, Gupta N. Phytase producing lactic acid bacteria: Cell factories for enhancing micronutrient bioavailability of phytate rich foods. Trends in Food Science & Technology. 1 févr 2020;96:1-12.

Development of yellow emissive carbon quantum dots with copper chelating activity from Dichrostachys golmerata

By Stève Djiazet (post-doctoral researcher)

Supervisors: Raphaël SCHNEIDER

Keywords Dichrostachys golmerata · Carbon quantum dots · Copper chelation · Yellow emission

PRODUCT ENGINEERING, EMMAD

General context, scientific issue

Some biological circulating ions can become toxic to cells, organs or the entire system. This is the case of circulating Cu2+ in high concentration, which has been associated to neurodegenerative and hepatic disorders and oxidative damages of biomolecules [1,2]. Antioxidants, including polyphenols and thiol-based antioxidants are presented as solution for the prevention and treatment of such pathologies [3,4]. Polyphenols are also proposed as a solution but their use as therapy against prooxidants may also have challenges like malabsorption or digestion disorder [5,6]. Carbon quantum dots (CQDs) appear as an alternative solution as they may exhibit antioxidant activity [7].

Objectives and stakes

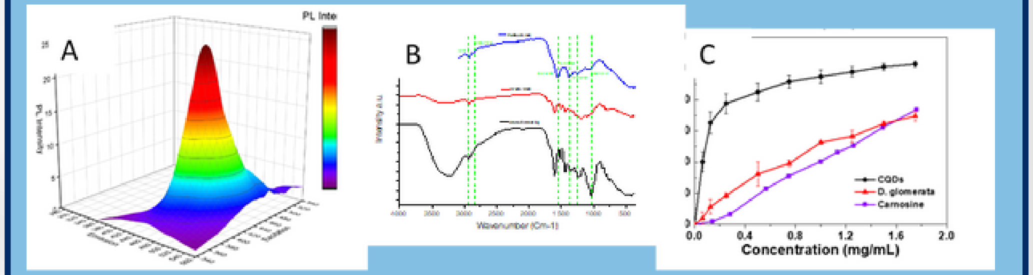
-Evaluate the effect of the excitation and emission wavelengths of CQDs.
-Determine the molecular bases responsible of the Cu2+ chelating activity of CQDs compared to the crude extract of D. glomerata.
-Evaluate the copper chelating activity of CQDs from D. glomerata.

References

[1] Moussa et al. (2018). ChemCatChem, 10, 4973-4983.
[2] Jiang et al. (2023). Biomolecules, 13, 143.
[3] Kuate et al. (2010). CyTA–Journal of Food, 8, 23-37.
[4] Kothari et al. (2014). Food and chemical toxicology, 69, 120-131.
[5] Karakaya et al. (2004). Critical reviews in food science and nutrition, 44, 453-464.
[6] Shahidi (2018). Journal of Food Bioactives, 4, 11-68.
[7] Moniruzzaman et al. (2022). Biomaterials Science, 10, 3527-3539.
[8] El-Hnayn et al. (2020). Nanomaterials, 10, 104-122.
[7] Shabbir et al. (2023). Inorganics, 11, 262-282.

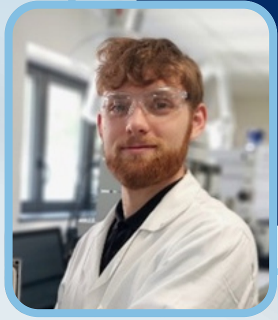
Methodology / Experimental approach

-The CQDs were prepared through a one pot hydrothermal synthesis method.
- After dialysis, CQDs were purified by dialysis, dried under vacuum and characterised by UV-visible absorbance and fluorescence spectroscopy, infrared spectroscopy,…
-The copper chelating activity was determined using the purified CQDs.



(A) 3D PL emission spectra of CQDs, (B) FT-IR spectra (CQDs, D. glomerata, crude extract of CQDs), (C) Copper chelating activity of CQDs, D. glomerata and carnosine.

Fig. A shows an emission within the green-yellow region (440 to 520 nm). The figure shows that the PL depends on the excitation wavelength with optimal excitation and emission wavelengths of 430 and 470 nm respectively. CQDs could therefore be used for bioimaging.
Fig. B is the FT-IR spectra of the starting extract of D. glomerata, crude and the purified CQDs. FT-IR results show that the functional groups present in the starting material are maintained in the purified CQDs. CQDs are enriched with carboxylate functional groups (stretchings at 1556 and 1371 cm-1) during the hydrothermal synthesis.
Fig. C demonstrates the Cu2+ chelating activity of CQDs, of the starting D. glomerata extract and of carnosine (used as reference). It shows a very fast chelating activity towards Cu2+ ions at very low concentration of CQDs (0.12 mg/mL). The chelating activity slows as from 0.2 mg/mL and becomes almost stable. The chelating activity of CQDs slowly increases above this value. At 1.75 mg/mL of CQDs, the chelating activity is 31.4% above that of the extract and Carnosine.
The fast and high Cu2+-chelating activity of CQDs can be explained by the high number of carboxylate functional group at their surface [8]. The carboxylate at the surface of CQDs interact through electrostatic interactions to sequester Cu2+ ions in solution [7]. The quasi-plateau reached above 0.4 mg/mL could be explained by the saturation of fixation sites of Cu2+ ions. The CQDs can therefore be used even at very small concentration for therapy related to accumulation of Cu2+ ions.



Enzymatic transformations of plant proteins to control the production of ingredients with calibrated functionalities

By Romain Faure (1st year)

Supervisors: Romain Kapel, Sophie Beaubier

Keywords Plant proteins Product Engineering Enzymatic crosslinking Transglutaminase Proteolysis Calibrated functionalities

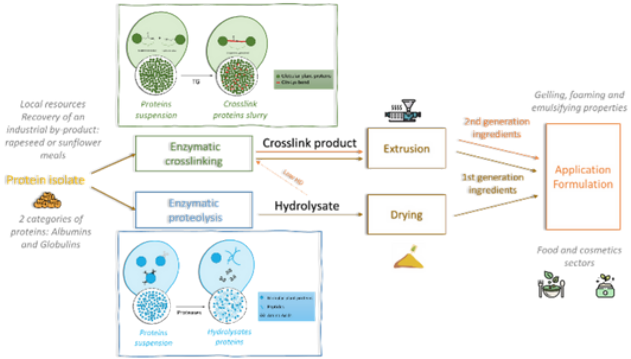
PRODUCT ENGINEERING

General context, scientific issue

Over the last few decades, plant proteins have been attracting increasing attention from industry, mainly because of their lower environmental impact than animal proteins. However, as a result of their lower functional properties, plant proteins have to be modified or processed.

Objectives and stakes

The aim of this thesis is to control the modification of the physical characteristics of plant proteins (solubility, charge, hydrophobicity, etc) in order to improve their functional properties (gelling, foaming and emulsifying properties). Improving their functional properties would allow their use in food products or cosmetic formulations to be developed and increased.



Scientific strategy for the enzymatic modification of plant proteins

Methodology / Experimental approach

To modify the physical characteristics of plant proteins, two promising and enzymatic processes will be studied, modelled and optimised. The first process is the enzymatic hydrolysis or proteolysis and the second process is enzymatic cross-linking. Enzymatic modifications of plant proteins were chosen because of their low environmental impact (mild conditions), and high specificity for their substrate, unlike physical (heat treatment, high pressure, etc) and chemical (glycosylation, acylation, etc) modifications.

Main results

Enzymatic hydrolysis is a process in which a protease breaks down proteins into a complex mixture of intact proteins, peptides and amino acids. This mixture generally has better foaming and emulsifying properties than native proteins, and significantly improved digestibility. In the case of enzymatic cross-linking, transglutaminase is used to cross-link proteins. The cross-linked products are composed of a few proteins up to several proteins, which create aggregates or even form a network. This network is covalent and the gel formed is a strong gel useful for meat-like products, for example.

Precise control of these processes is crucial for modelling the production of functional products with calibrated properties. The first part of this thesis will therefore focus on the development of an original analysis technique for monitoring the enzymatic cross-linking process. This will be followed by an advanced analysis of the physical characteristics of the cross-linked products. Then, particular attention will be paid to the possible precipitation of certain cross-linked products by monitoring the appearance of insoluble particles by transmittance measurements.

References

[1] Djoullah A. et al., Food Hydrocolloids, 2018, 77:636-645.
[2] Beaubier S. et al., Foods, 2021, 10:664.
[3] Zhang L. et al., LWT, 2022, 153:112415

Synthesis of core/shell TiO2/CeO2 nanoparticles to increase drugs photostability

By Michał Gackowski (PhD Candidate, 1st year)
Supervisors: Raphaël Schneider, Tomasz Osmałek

Keywords Titanium dioxide · Cerium dioxide · Photostability · Photodegradation · Crystal violet · Voriconazole · Phototoxicity

PRODUCT ENGINEERING

General context, scientific issue

TiO2 nanoparticles are a protective shield for drugs vulnerable to electromagnetic radiation-induced degradation. This shielding effect is particularly significant for drugs applied topically, helping to prevent the formation of toxic metabolites due to drug transformation under radiation exposure.

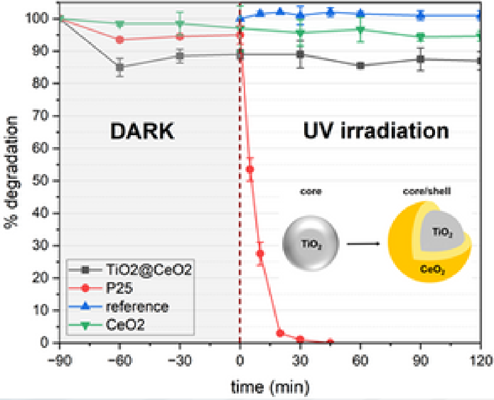
Objectives and stakes

This study aims to synthesize modified titanium(IV) oxide nanoparticles with reduced photocatalytic activity and a broad ultraviolet absorption range. The synthesized nanoparticles will be used to prepare a drug formulation for voriconazole for transdermal delivery. The addition of sunscreen to the formulation of the drug is expected to prevent the degradation of the drug when exposed to radiation.

Methodology / Experimental approach

In the initial study, a commercially available material with high photocatalytic activity - Degussa's TiO2 p25 - was coated with a cerium-based metal-organic framework. The objective is to create a core/shell structure. The formed product is then calcinated to produce a cerium(IV) oxide coating at the surface of TiO2. Cerium(IV) oxide CeO2 was selected as the coating material because of (i) its absorption spectrum shifted towards higher wavelengths relative to TiO2 and (ii) its antioxidant properties.
The primary test for determining the photocatalytic activity of a material is to study the decomposition of an organic dye under irradiation with light in the presence of a catalyst.

As part of the study, the potential of TiO2@CeO2 nanoparticles to produce reactive oxygen radicals (ROS), including singlet oxygen, superoxide anion, hydrogen peroxide, and hydroxyl radical, was also evaluated. The material was characterized using techniques such as X-ray diffraction, Diffuse Reflectance Spectroscopy, Electron Paramagnetic Spectroscopy, Fourier-transform Infrared Spectroscopy, surface area according to Brunauer-Emmett-Teller (BET) theory, Scanning Electron Microscope, and Transmission Electron Microscopy.



Photocatalytic degradation of Crystal Violet (5 mg/L) in the presence of catalysts under electromagnetic radiation (Hg-Xe lamp; light intensity = 20 mW.cm-2). The reference corresponds to the dye stability in the absence of the catalyst. P25 - TiO2 p25 Degussa.

Main results

Based on the Crystal Violet (CV) photocatalytic decomposition study, the catalytic activity of TiO2 P25 was inhibited after coating CeO2 on its surface. A relatively weak adsorption of CV (ca. 10%) is observed during the 90 minutes of stirring in the dark. No significant degradation of CV is observed under UV light irradiation. This was confirmed by ROS detection: hydroxyl and superoxide anion radicals, as well as singlet oxygen radicals, could not be detected for TiO2@CeO2 nanoparticles, while all these species are produced by pure TiO2.
XRD and transmission electron microscopy will be used to determine the size and shape of the TiO2@CeO2 particles produced. We will also investigate the photostability under UV light illumination of voriconazole, our objectives being to demonstrate that TiO2@CeO2 nanoparticles can enhance the stability of this drug.
Accelerated stability testing of the material (according to ICH guidelines) and cytotoxicity of the material using the Microtox® test will also be conducted.

References

[1] Gackowski M, Osmałek T, Froelich A, Otto F, Schneider R, Lulek J. Phototoxic or Photoprotective?—Advances and Limitations of Titanium (IV) Oxide in Dermal Formulations—A Review. International Journal of Molecular Sciences. 2023; 24(9):8159.
[2] Lodén M, Akerström U, Lindahl K, Berne B. Novel method for studying photolability of topical formulations: a case study of titanium dioxide stabilization of ketoprofen. J Pharm Sci. 2005;94(4):781-787.
[3] Smijs TG, Pavel S. Titanium dioxide and zinc oxide nanoparticles in sunscreens: focus on their safety and effectiveness. Nanotechnol Sci Appl. 2011;4:95-112.
[4] Racovita AD. Titanium Dioxide: Structure, Impact, and Toxicity. International Journal of Environmental Research and Public Health. 2022; 19(9):5681.

Development and design of new hybrid materials of the “MOFs” type with advanced functionalities for removal of micropollutants from water

By Ola Haidar (3rd year)

Supervisors: Thibault Roques-Carmes, Joumana Toufaily, Mohamad Hmadeh

Keywords Zirconium metal-organic frameworks | Water purification | Structural defects | Micropolluants

PRODUCT ENGINEERING

General context, scientific issue

Micropollutants are residual compounds found in wastewater from sources including households, industries, hospitals, agricultural activities, and livestock farming. These contaminants are not eliminated by wastewater treatment processes, posing significant dangers to water quality(1)(2).

Objectives and stakes

In this study, the effective removal of three major micropollutants (e.g., propranolol hydrochloride, 1-naphthylamine, and 2-naphthol) from water is investigated using defected UiO-66 and functionalized derivatives as adsorbents.

Methodology / Experimental approach

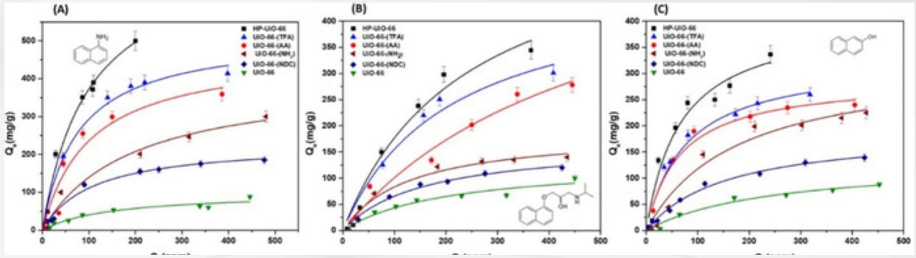
Defect-rich MOFs structures are prepared for the removal of the three micropollutants using two approaches, the first one is based on labilization of linker, for the creation of hierarchically porous metal–organic framework (HP-UiO-66). The second strategy involves a modulation synthesis using Acetic acid/Trifluoro acetic acid as two types of modulators, and their impact on the structural characteristics of the produced MOF nanoparticles is thoroughly explored.

To better understand the process of adsorption and the interactions between the micropollutants and the MOF adsorbents, all MOFs are compared to the ideal nonmodulated UiO-66 MOF, the amino-functionalized terephthalic acid (H2BDC-NH2), and the naphthalene-based UiO-66 structures.

Main results

The different UiO-66-based structures showed different performances with 1-Naphthylamine (1-NA), propranolol hydrochloride (PPL) and 2-Naphthol (2-NO). The adsorption isotherm experiments were carried out at a series of concentrations (10, 30, 60,100,200,300,400,500 and 700 ppm) of solutions of 4 ml of the pollutant with 4 mg of adsorbent for 24 h. The three best performing MOFs were HP-UiO-66, UiO-66-(AA) and UiO-66-(TFA).

The adsorption capacity of the most efficient MOFs was further investigated using adsorption isotherms of 1-NA, PPL and 2-NO at a wide range of concentrations, as shown in the figure . To further study the effect of structural defects in contaminant adsorption and adsorption mechanism, other UiO-66 frameworks were introduced for reference to discuss. This includes a naphthalene-substituted UiO-66, called UiO-66-(NDC), which is synthesized using 2,6-naphthalenedicarboxylic acid as a ligand, as well as a UiO-66 functionalized with (NH2), UiO-66-(NH2).



Langmuir model adapted to the adsorption isotherms of 1-NA (A), PPL (B) and 2-NO (C) on UiO-66 adsorbents. The points correspond to the experimental data and the lines correspond to the model fitting results.

References

1. Montagner CC, Vidal C, Acayaba RD. Contaminantes emergentes em matrizes aquáticas do Brasil: Cenário atual e aspectos analíticos, ecotoxicológicos e regulatórios. Quim Nova. 2017;40:1094–110.
2. Ayoub H, Roques-Carmes T, Potier O, Koubaissy B, Pontvianne S, Lenouvel A, et al. Comparison of the removal of 21 micropollutants at actual concentration from river water using photocatalysis and photo-Fenton. SN Appl Sci. 2019;1:1–12.

Design and Preparation of Bio-based Itaconate Elastomer Composites with a Broad Damping Temperature Range and High Performances

By Fulan HAO, 3rd year

Supervisors: Laurent FALK, Liqun ZHANG

Keywords Preparation process | Bio-based itaconate elastomers | Rubber Composites | Damping Performance | Physical properties

PRODUCT ENGINEERING

General context, scientific issue

Vibration and noise not only harm people's physical and mental health but also seriously affect the stability and reliability of mechanical equipment operation. Among the numerous methods for reducing vibration and noise, the preparation of high-performance polymer damping materials is a key solution due to their viscoelastic properties, which can absorb vibration mechanical energy and dissipate it as heat energy.[1-3] The loss tangent (tan δ), defined as the ratio of loss modulus (E”) to storage modulus (E’), measures the dissipation of vibration energy.[4] High-performance damping materials should exhibit a high loss factor (tan δ > 0.3) over a broad temperature range of at least 60-80°C.[5] The damping properties of rubber materials are determined by their inherent hysteresis loss, which increases with the internal friction between molecular chains. There has been limited research on environmentally friendly polymer damping materials. Recently, a bio-based itaconate elastomer was synthesized through environmentally benign emulsion polymerization of bio-based dibutyl itaconate with butadiene. This elastomer contains curable double bonds and numerous side ester groups attached to the polymer backbone, and has demonstrated good physical and damping properties.[6,7] However, this homopolymer typically only shows effective damping performance below room temperature with a narrow temperature range of 20–30°C, which is insufficient for many applications. Therefore, developing bio-based elastomer composites with a high loss factor at room temperature and a wide damping temperature range through blending and modification methods is a crucial and challenging task.

Objectives and stakes

1.Clarify the damping mechanism by studying the relationship between the microstructure and properties of bio-based elastomers.
2.Provide theoretical guidance and design principles for developing new bio-based elastomers with high damping performance.

Methodology / Experimental approach

1.Bio-based itaconate elastomers with varying contents of diethyl itaconate were synthesized.
2.The impact of diethyl itaconate content on the damping properties will be studied.
The PDEIB copolymers of diethyl itaconate and butadiene were prepared by emulsion polymerization in a vertical kettle. Here, PDEIB30, PDEIB40, PDEIB50, PDEIB60, and PDEIB70 correspond to mass amounts of butadiene at 30 wt%, 40 wt%, 50 wt%, 60 wt%, and 70 wt%, respectively. A representative procedure for the preparation of PDEIB60 is described as an example.

First, 15 g of emulsifier, 800 g of deionized water, 0.85 g of activator, 2.8 g of electrolyte, 0.6 g of molecular weight regulator, 0.2 g of deoxidizer, and 160 g of diethyl itaconate were added into the kettle. Second, 240 g of butadiene was injected into the kettle. Third, the polymerization started at 6°C when 0.36 g of initiator was injected into the pre-emulsion. The homogeneous and stable PDEIB latex was obtained after 5 hours. Finally, the PDEIB latex was demulsified with ethanol to obtain the PDEIB gum, which was then dried in an oven at 50°C until a constant weight was achieved.

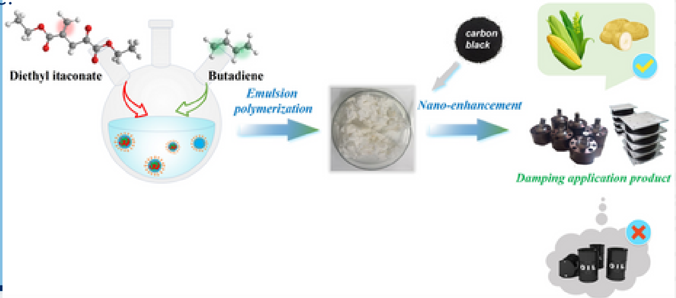


Fig. 1- Prototype of the microfluidic system perfused with colorant. A concentration gradient is apparent.

Main results

Figure 1 shows the tan δ versus temperature curves for the filled PDEIB composites. As the mass amount of diethyl itaconate increases, the loss factor tan δ rises, the damping temperature shifts to a higher value, and the damping temperature range broadens compared to the PDEIB70 composites. Overall, the damping temperature range for PDEIB composites extends from 42 to 61 ℃ , demonstrating that the diethyl itaconate content can broaden the damping temperature range of PDEIB composites.

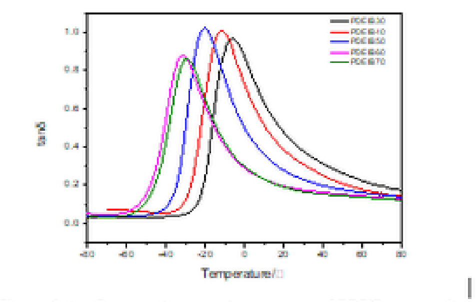


Figure 1. tanδ versus temperature curves of PDEIB composites

References

[1] Y. Pan, et al. Polym.-Plast. Tech.Mat. 59 (4) (2019) 385–397.
[2] J. Zhu et al. Polymer 155 (2018) 152–167.
[3] L. Zhu et al. Polymer Testing 93 (2021), 106885.
[4] Y.C.Zhu et al. J.Phys. Chem. B 2007, 111, 11388-11392.
[5] X. Lu et al. Polym. Adv. Technol. 2014, 25 21-28.
[6] XX. Zhou et al.Polym. Chem., 2019, 10, 6131–6144.
[7] XX. Zhou et al. Pure and Applied Chemistry, 2015, 87(8), 767-777.

0D/1D CuO-Cu2O/ZnO p-n heterojunction with high photocatalytic activity for the degradation for of dyes and Naproxen

By Mouna IBN MAHRSI (PhD student)
Supervisors: Raphaël SCHNEIDER

Keywords Heterostructured photocatalyst | CuO-Cu2O/ZnO | Photocatalytic degradation | Naproxen

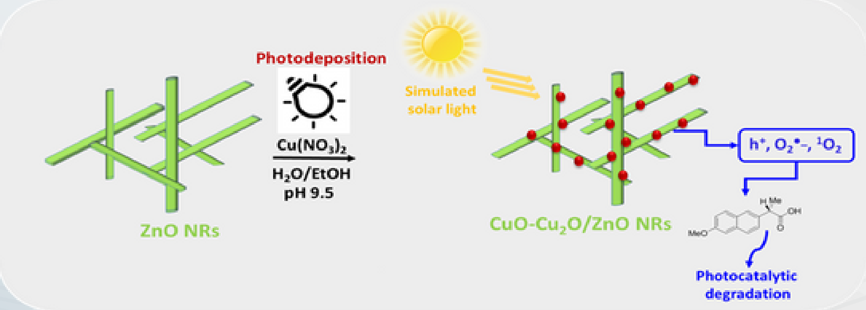
PRODUCT ENGINEERING

General context, scientific issue

ZnO is a well-known n-type semiconductor exhibiting a high photocatalytic activity, low cost and weak toxicity and has therefore found many environmental applications [1]. However, ZnO exhibits drawbacks like the fast recombination of electron/hole pairs and the weak absorption of visible photons (energy bandgap of 3.3 eV) which restrict its photocatalytic activity [2]. Among the strategies developed to overcome these disadvantages are the doping of ZnO with metals or non-metals [3] or the construction of heterojunctions with smaller bandgap semiconductors that allows mutual transfer of charge carriers [4]. CuO and Cu2O are p-type low bandgap semiconductors (ca. 1.85 and 2.0–2.2 eV for bulk CuO and Cu2O, respectively) [5] that can be coupled to ZnO to form p-n heterostructures that allow to decrease the electron/hole recombination and increase the visible light response.

Methodology / Experimental approach

The photodeposition of CuO-Cu2O particles onto the surface of ZnO NRs was conducted by irradiating a dispersion of ZnO NRs and Cu(NO3)2 with a 150 W Xe lamp.
The photocatalysts prepared were characterized by TEM, SEM, XRD, diffuse reflectance spectroscopy.
The products generated during the photocatalytic degradation of Naproxen were investigated by LC UV/(+) MS2.



Schematic illustration of the CuO-Cu2O/ZnO photocatalyst synthesis and of its use for the degradation of Naproxen

Objectives and stakes

Our objectives are:
(i) Design of a new heterostructured photocatalyst through the construction of a p-n heterojunction between ZnO and CuO-Cu2O nanoparticles.
(ii) Analyze the impact 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 photacatalytic activity.
(v) Evaluate the stability of the photocatalysts.

Main results

p-n CuO-Cu2O/ZnO heterostructured photocatalysts were prepared via a facile and green photodeposition route and successfully used for the degradation of anionic and cationic dyes (RhB, RBBR) and Naproxen under simulated solar light irradiation. The structural characterizations show that the photodeposition route allows the association of ca. 2.4 nm-sized CuO-Cu2O particles of monoclinic structure with wurtzite ZnO nanorods. The high photocatalytic performance of the CuO-Cu2O(10%)/ZnO photocatalyst originates both from the p-n heterojunction which allows to expand the visible light absorption and from the decreased recombination rate of photogenerated charge carriers. Its high performance combined with its high stability make the CuO-Cu2O(10%)/ZnO photocatalyst of high potential for environmental remediation.

References

[1] C. Boon Ong, L. Yong Ng, A. Wahab Mohammad. A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications. Renew. Sust. Energ. Rev. 81 (2018) 536-551.
[2] M. Ibn Mahrsi, B. Chouchene, T. Gries, V. Carré, E. Girot, G. Medjahdi, F. Ayari, L. Balan, R. Schneider. Novel ZnO/Ag nanohybrids prepared from Ag+-doped layered zinc hydroxides as highly active photocatalysts for the degradation of dyes and Ciprofloxacin. Colloids Surf. A: Physicochem. Eng. Asp. 671 (2023) 131643.
[3]] F. Achouri, S. Corbel, L. Balan, K. Mozet, E. Girot, G. Medjahdi, M. Ben Said, A. Ghrabi, R. Schneider. Porous Mn-doped ZnO nanoparticles for enhanced solar and visible light photocatalysis. Mater. Des. 101 (2016) 309-316.
[4] S. Goktas, A. Goktas. A comparative study on recent progress in efficient ZnO based nanocomposite and heterojunction photocatalysts: A review. J. Alloys Compd. 863 (2021) 158734.
[5] D.S. Murali, S. Kumar, R.J. Choudhary, A.D. Wadikar, M.K. Jain A. Subrahmanyam. Synthesis of Cu2O from CuO thin films: Optical and electrical properties. AIP Adv. 5 (2015) 047143.

Synthesis and biological activity of NO-donor amidoximes

By Lilian Karcher, 1st year

Supervisors: Raphaël Schneider, Axelle Arrault

Keywords Amidoximes Pyrrole Pyridine NO donor

PRODUCT ENGINEERING, LCPM

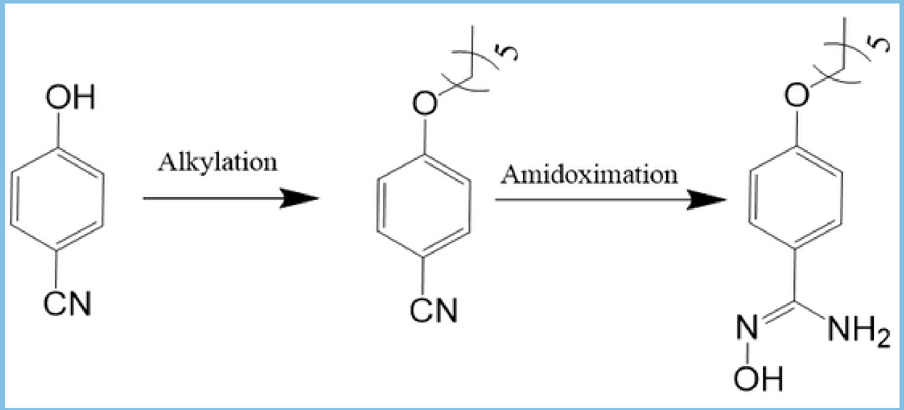
General context, scientific issue

Amidoximes, oximes in which one of the substituents is an amino group, exhibit a crucial role in human physiology, particularly as nitric oxide NO precursors which presents many beneficial biological effects, in particular on the cardiovascular system [1]. Amidoxime prodrugs have been effective in treating cardiovascular disorders, reducing blood pressure, inhibiting platelet aggregation, and inducing vasorelaxation in vitro [2]. The development of external sources to increase the NO level in the body, for example by using amidoximes and oximes which can be oxidized in vivo and release NO, is currently the subject of much research.

Methodology / Experimental approach

The first part of this work focuses on the development of new aromatic or heteroaromatic mono or polyamidoximes and particularly of compounds containing the pyrrolo[2,3-d]pyrimidine motif. The structure of the substituents on the aromatic rings will be varied to control the LogP value (ideally between 1.4-1.8) for good oral and intestinal absorption.

Later, a second nitrile function will be introduced on the alkyl chain to prepare bis-amidoximes whose NO donor potential has been demonstrated in a previous work of the group [1].



Synthesis of amidoximes from 4-cyanophenol

Objectives and stakes

The first part of this PhD involves the synthesis of aromatic and heteroaromatic amidoximes.

The second part will involve testing the ability of amidoximes to release NO in vitro (rat liver microsomes, human cells) followed by cytocompatibility tests.

Third part is the encapsulation of amidoximes to control the supply of NO.

The last part is the analysis and the impact of metabolites generated by amidoximes on the environment, particularly for the bacterial populations present in the wastewater.

Main results

The alkylation and amidoximation of cyanophenol were first undertaken. 4-Cyanophenol reacts with 1-bromohexane in the presence of K_2CO_3 to afforded 4-(hexyloxy)benzonitrile in 96% yield. The resulting product was mixed with $NH_2OH.HCl$ and DIPEA to give the corresponding amidoxime in 63% yield.

Synthetic conditions were optimized under microwave radiation by varying the power (90, 100 and 180 W), the base (K_2CO_3, Et_3N, DIPEA) and the reaction time (between 12 and 18 min irradiation) [3]. Results showed that triethylamine is the most appropriate base for the amidoximation reaction and that a mild power of 100 W allows a marked decrease of the reaction time (15 min vs 19 h using a conventional thermal heating). The methodology was extended to 3-cyanopyridine and 3-cyanopyridine N-oxide and the corresponding amidoximes were obtained in high yields (> 90%).

The synthesis of bis- and tris-amidoximes with adequate logP values is currently under study to reduce the concentration of the drug administered without altering biological activity.

References

[1] Sahyoun, T.; Arrault, A.; Schneider, R. Amidoximes and Oximes: Synthesis, Structure, and Their Key Role as NO Donors. Molecules2019, 24 (13), 2470

[2] Mansuy, D.; Boucher, J. L.; Clement, B. On the Mechanism of Nitric Oxide Formation upon Oxidative Cleavage of C=N(OH) Bonds by NO-Synthases and Cytochromes P450. Biochimie 1995, 77 (7–8), 661–667.

[3] Albayati, M. R.; Mohamed, M. F. A.; Moustafa, A. H. Optimization of the Synthesis of Het/Aryl-Amidoximes Using an Efficient Green Chemistry. Synthetic Communications 2020, 50 (8), 1217–1231.

Sustainable and continuous production of phenolic acids by enzymatic nanofiltration reactor for the valorization of effluents from oleoproteaginous protein production

By Fatima Zahra KDAH, 2st year
Supervisors: Romain KAPEL, Jean-Pol Frippiat

Keywords By-product valorization | Antioxidant and anti-inflammatory bioactivity | Polyphenols | Ion exchange adsorption | Membrane enzymatic reactors

PRODUCT ENGINEERING, SIMPA

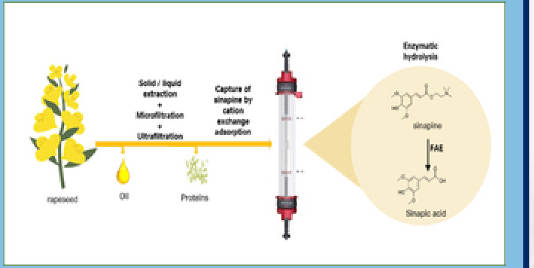
General context, scientific issue

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]

Methodology / Experimental approach

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.



General strategy for the valorization of the by-products of oilseed protein production

Objectives and stakes

The aim of this thesis project is to develop a process coupling adsorption, enzymatic 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.
In the 1st year, we were particularly interested in the screening of different cation exchange resins and finding the optimal mixture of sinapine/sinapic acid having the best biological activities. In the 2nd year, the objective is to study the adsorption and desorption batch (kinetics and thermodynamics), and continuous to determine the optimal conditions to purify sinapine. In this year, we are interested in the investigation of enzymatic hydrolysis of sinapine coupled to adsorption.

Main results

1. Phenolic ester batch adsorption and desorption using cation exchange resin: a resin-pH condition was selected based on the adsorption and desorption rates, kinetics and the stability of phenolic compounds.1.1. Adsorption kinetic study: The equilibrium time for each resin was determined. The adsorption kinetics followed a pseudo-second-order model.1.2. Adsorption thermodynamic study: the isotherms data better fitted Langmuir model the adsorption process was spontaneous and exothermic. 1.3. Desorption study: A two-step desorption using 2 ethanolic solutions yielded highly purified phenolic ester target (98.85%). 2. Continuous adsorption/desorption: The optimal adsorption flow rate was determined. Based on a design of experiment, the optimal composition of desorbing solution was identified. Further tests will determine the optimal desorption rate. 3.The investigation of enzymatic hydrolysis to improve antioxidant activity [3]: A commercial enzyme was selected following an enzyme screening based on sinapoyl esterase activity. The study of the enzymatic kinetics is initiated. Hydrolysis tests of the phenolic ester adsorbed on cation exchange resin will be performed to evaluate the effect on the activity of the enzyme.

References

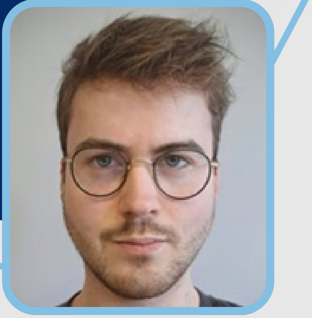
[1] Albe Slabi, Sara, Christelle Mathé, Xavier Framboisier, Claire Defaix, Odile Mesieres, Olivier Galet, et Romain Kapel. « A New SE-HPLC Method for Simultaneous Quantification of Proteins and Main Phenolic Compounds from Sunflower Meal Aqueous Extracts ». Analytical and Bioanalytical Chemistry 411, no 10 (avril 2019): 2089-99. https://doi.org/10.1007/s00216-019-01635-2.
[2] Le, Tuong Thi, Xavier Framboisier, Arnaud Aymes, Armelle Ropars, Jean-Pol Frippiat, et Romain Kapel. « Identification and Capture of Phenolic Compounds from a Rapeseed Meal Protein Isolate Production Process By-Product by Macroporous Resin and Valorization Their Antioxidant Properties ». Molecules 26, no 19 (27 septembre 2021): 5853. https://doi.org/10.3390/molecules26195853.
[3] Wu, C, M Huang, Y Lin, H Ju, et H Ching. « Antioxidant Properties of Cortex Fraxini and Its Simple Coumarins ». Food Chemistry 104, no 4 (2007): 1464-71. https://doi.org/10.1016/j.foodchem.2007.02.023.

Solvent-free electrode manufacturing using electrostatic spray deposition: process optimization and modelling

By Alex Lemarinel, 1st year

Supervisors: Véronique Falk, Maria Graciela Cares, Thomas Philippe (Ampère)

Keywords Powder mixtures Lithium-ion battery Solvent-free electrode Electrostatic spray deposition



PRODUCT ENGINEERING, AMPÈRE

General context, scientific issue

Even though lithium-ion battery is widely used as energy storage system for numerous applications including transport, the industrial electrode manufacturing process suffers from poor energy efficiency, which stands for energy waste and cell extra cost. The energy required to manufacture a cell can be significantly reduced by eliminating solvents, which are responsible for two energy-consuming steps : evaporation and distillation [1].

Methodology / Experimental approach

Identifying the most influential parameters and meaningful measures to characterize electrode performance is crucial. Due to the many multiscale parameters (from particle to bulk to processing), the design of experiments method is chosen to determine the influence of electrode materials and process parameters on electrode performance. This method is expected to provide better control over the process and to improve electrodes electrochemical performance.

Among the studied parameters it is possible to highlight:

-Powder physico-chemical properties: This includes shape, particles size distribution, true density, and surface energy.

-Mixing parameters: Such as mixer type, mixing speed, or mixing time.

-Powder minimum fluidization velocity: This parameter describes the dynamic behavior of powders and can be used as a descriptor of deposition homogeneity.

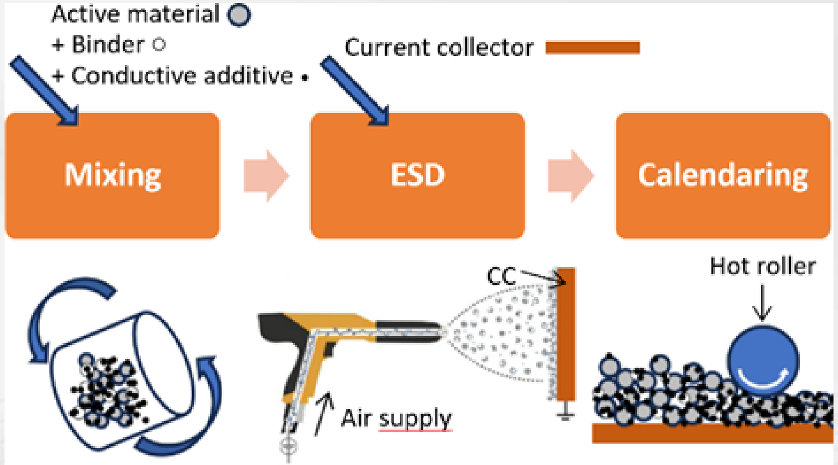
-Charge-to-mass ratio: Measured to ensure good particles deposition on the CC during electrostatic spray deposition.

-Film adhesion on the CC: Estimated using peeling and pull-off tests after thermal activation and calendaring.

The main objective is to manufacture high-performance electrodes. Thus, different standard tests are conducted on half-cells or full cells, including successive charging/discharging cycles at different currents, electrochemical impedance spectroscopy, cyclic voltammetry, or even electrode tortuosity determination using symmetrical cell. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy analysis (SEM-EDS) is also performed to correlate microstructures with electrode electrochemical performance.

Objectives and stakes

Within solvent-free processes, the one based on electrostatic spray deposition (ESD) of electrode powdered materials, which consists in the deposition of charged and fluidized particles on a current collector (CC), shows potential for high-performance electrode manufacturing [2], including for electric mobility purposes. However, obtaining reproductible electrodes remains a challenge, this requirement being highly dependent on the behavior of powders within each unit operation: mixing, ESD and calendaring (see illustration). Finding adequate formulation and process parameters is key to scaling this process successfully [3].



Block-diagram of the process based on of electrostatic deposition (ESD) of powder mixture for electrode manufacturing

References

[1] Zhang Y. et al., Renew. Sustain. Energy Rev. 2023, 183: 113515.
[2] Degen F. et al., IEEE Trans. Eng. Manag. 2024, 71: 1038–1056.
[3] Wang M. et al., J. Electrochem. Soc. 2023, 170: 010541.

Molecular design, synthesis and process development of bio-based functional elastomers

By Liwei LI, 3rd year
Supervisors: Guo-Hua HU, Liqun ZHANG

Keywords Bio-based carboxylated itaconate elastomers | Zinc oxide | Ionic crosslinking

PRODUCT ENGINEERING

General context, scientific issue

The carboxylated itaconate (PDBIBA) elastomer is an ionomer containing carboxyl functional groups, derived from the polymerization of dibutyl itaconate (DBI), butadiene (BD), and methacrylic acid (MAA). These elastomers possess both double bonds and carboxyl groups, making them potentially reactive. Consequently, PDBIBA elastomers can undergo crosslinking not only via the double bonds using traditional agents like sulfur or peroxide but also through ionic interactions involving carboxylic groups and metal oxides such as zinc oxide or magnesium oxide. For instance, significant salt-bonding occurs in polymerized Zn2+ or Mg2+-based unsaturated carboxylic acid salt molecules due to strong electrostatic interactions. These interactions can restrict the mobility of nearby rubber chains while concurrently yielding high modulus ion clusters, thus serving as effective reinforcing agents [1, 2].

Methodology / Experimental approach

The carboxylated itaconate elastomer contains 7.6 wt % carboxylic groups (-COOH). The vulcanization system relies on zinc oxide to form ionic cross-links. Compounds comprising carboxylated itaconate elastomer and zinc oxide are prepared in varying proportions of zinc oxide: 2, 3.6, 5, 10, and 15 phr, with 3.6 phr being the stoichiometric concentration required to neutralize the carboxylic acid groups. The samples are named accordingly, such as ZnO-2, denoting the vulcanizing agent (ZnO) and its amount (in phr).

The PDBIBA compounds are prepared as follows: Initially, PDBIBA compounds are mixed on a two-roll mill featuring a cylinder diameter of 15 cm, a length of 30 cm, and a friction ratio of 1:1.2. The rolls are maintained at a low temperature during the mixing process by circulating cold water through them. After mixing for 20 minutes, the PDBIBA compounds are obtained. Subsequently, the compounds are hot compression molded into 1 mm-thick sheets at 150°C under 15 MPa for 20 minutes.

Finally, FTIR spectra of the PDBIBA elastomers are acquired using a Bruker Tensor 27 spectrometer (Bruker, Germany) under specific conditions: wavenumber range of 600-4000 cm-1 and a resolution of 4.0 cm-1.

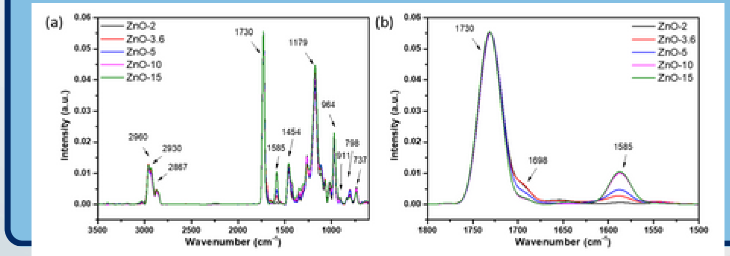


Figure 1. (a) FTIR spectra of PDBIBA elastomers with different ZnO contents. (b) Magnified portion from 1500 cm-1 to 1800 cm-1.

References

[1] Debdipta B. et al. Macromolecules. 2014, 47: 3436-3450.
[2] Chuanhui X. et al. ACS Sustainable Chem. Eng. 2016, 4: 6981-6990.
[3] Ibarra L. et al. J. Appl. Polym. Sci. 2008, 108: 2197-2205.

Objectives and stakes

During the molding process of carboxylated itaconate elastomers in the presence of metal oxides, the formation of carboxylic acid salts occurs, leading to the development of ionic elastomers or ionomers with significantly enhanced physical properties. This project aims to cross-link carboxylated itaconate elastomers using zinc oxide, analyze the reaction process between carboxylated itaconate elastomers and zinc oxide through FTIR spectroscopy, and explore the influence of zinc oxide concentration and cross-linking temperature on the resulting cross-linked carboxylated itaconate elastomers.

Main results

Figure 1 (a) depicts the FTIR spectra of PDBIBA elastomers with varying ZnO contents. The broad absorption peaks at 2960, 2930, and 2867 cm-1 are ascribed to the stretching vibrations of -CH3, -CH2, and -CH in the terpolymers. Peaks at 1730 cm-1 represent the C=O stretching vibrations of dibutyl itaconate and methacrylic acid, respectively. The peaks at 1454 cm-1 correspond to the deformation vibration of -CH3 and -CH2. Peaks at 1179 cm-1 belong to the C−O−C stretching vibrations of dibutyl itaconate. Peaks at 798 cm-1 correspond to the C-O-C deformation vibration of dibutyl itaconate. Peaks at 737 and 964 cm-1 correspond to the C−H deformation vibration of the cis-1,4 structures and trans-1,4 structures of butadiene, respectively. Peaks at 911 cm-1 correspond to the C−H deformation vibration of the 1,2 vinyl structures of butadiene.

The carbonyl region in the wavenumber range of 1500-1800 cm-1, as shown in Figure 1 (b), is relevant for understanding the status of ionic associations in the networks. Peaks at 1730 and 1698 cm-1 are evident for all samples, corresponding to C=O stretching vibrations and dimeric linkages of the carboxyl. Upon the incorporation of ZnO, the reaction of the −COOH group of PDBIBA with ZnO results in predominantly zinc carboxylate formation, represented by a peak at 1585 cm-1 [3]. Upon cross-linking with ZnO, the peak intensity of the dimeric linkages of the carboxyl is significantly reduced with increasing ZnO content, while the peak intensity corresponding to the zinc carboxylate structure gradually increases.To understand the impact of ZnO content on the peak area under the peak (a measure of its intensity), a Gaussian function is fitted, and the results are presented in Table 1.

Table 1. Curve fitting results for 1698 and 1585 cm^{-1}

Wavenumber (cm^{-1})	Area				
	ZnO-2	ZnO-3.6	ZnO-5	ZnO-10	ZnO-15
1698	0.11	0.10	0.05	0.04	0.02
1585	0.03	0.10	0.18	0.32	0.32

To understand the impact of ZnO content on the peak area under the peak (a measure of its intensity), a Gaussian function is fitted, and the results are presented in Table 1. The relative peak area of the 1698 cm^-1 peak decreases monotonically from 0.11 to 0.02 as the ZnO content increases from 2 to 15 phr. Conversely, that of the 1585 cm^-1 peak increases monotonically from 0.03 to 0.32 with increasing ZnO content from 2 to 10 phr, plateauing at higher ZnO contents of 10 and 15 phr. This observation suggests that the production of zinc carboxylate from excess zinc oxide with carboxyl groups becomes limited at a certain carboxyl group content.

Development and optimization of innovative processes of protein ingredients production from lentils and chickpeas

By Odile Mesieres, 1st year

Supervisors: Véronique Sadtler, Sophie Beaubier, Romain Kapel

Keywords
Legumes
Pulses
Plant protein
Protein ingredient
Fractionation processes
Functional properties

PRODUCT ENGINEERING, GPBF

General context, scientific issue

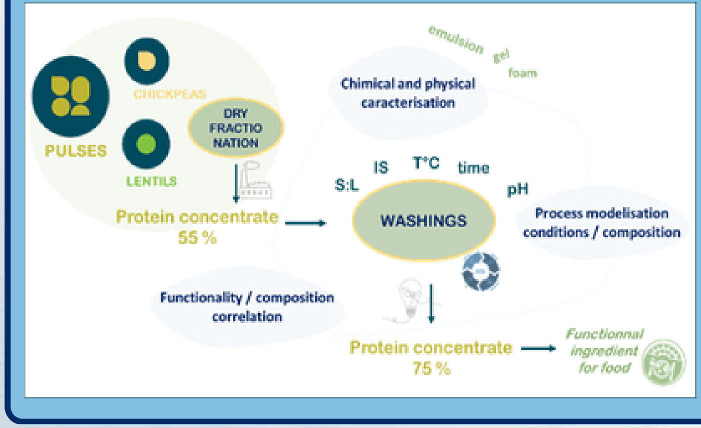
In recent years, the demand for alternative proteins increased and legumes seem to meet this need. Indeed, lentils and chickpeas are a good source of plant proteins. Despite a good nutritional profile, these pulses contain molecules which have a negative impact on their nutritional, functional or organoleptic quality. The main technological lever will therefore be the elimination of anti-nutritional factors through fractionation processes. [1-4]

Methodology / Experimental approach

Products from dry fractionation will be characterized by determining their composition and functional properties. An experimental plan will design a multiparametric study of washings of these ingredients and production conditions of protein ingredients by combination of dry fractionation and washing will be selected.

The optimization of the production of multi-use protein ingredients will be studied with modeling the impact of the washing conditions of the dry process product on classic performance criteria for protein ingredients. The optimum production of protein ingredients by combination of processes will be established using correlation models associated with multi-criteria optimization tools and decision-making engineering.

Finally, a life cycle analysis will be applied to minimize the environmental impact of this process.



Production of a protein concentrate by an innovative combination of dry fractionation and washing

Objectives and stakes

The main objective of this project is to develop and optimize innovative processes for production of protein ingredients from chickpeas and lentils through original combinations of dry fractionation and washings. Protein ingredients will must be suitable for targeted food processing and the process of production will be controled to meet a set of performance criteria and and low environemental impact.

Main results

Classically, legume protein products have a protein titer of around 55%. The idea is to develop an innovative process for producing protein concentrate approaching 75% with good functional properties for the food industry.

The first part of this thesis aims to determine the effect of dry fractionation on the composition and functional properties of ingredients produced in industry and to select the ingredients to be washed. An experimental design will be carried out in order to determine the optimal washing conditions to obtain the protein concentrate (75%) by eliminating antinutritional factors (tryptic inhibitors, saponins, GOS, phytic acid, lectins, tannins), while improving the functional properties : foaming, gelling and emulsifying, [3] and in vitro digestibility.

References

[1] M.A.I. Schutyser et al., Food Science & Technology. 2015, 45:327-335
[2] M. Vogelsang-O'Dwyer et al., Food Science & Technology. 2021, 110:364-374
[3] J.I. Boye et al., Food Research International. 2010, 43:537-546
[4] Manoj Kumar Pulivarthi et al., Wiley. 2023, 22:4670–4697

Photoproduction of green hydrogen using shaped MOFs

By Sher Mohd (1st year Ph.D.)
Supervisors: Raphaël SCHNEIDER, Véronique FALK

Keywords MOFs Photocatalysts Hydrogen Formatting

PRODUCT ENGINEERING

General context, scientific issue

The global population and economy's growth, alongside rapid urbanization, have sharply increased energy demand, primarily met by fossil fuels, emitting greenhouse gases and aggravating climate change. Shifting to sustainable energy is crucial for long-term global sustainability and security, requiring a move from carbon-intensive fuels to renewables like solar, wind, hydro, and geothermal power. Hydrogen production through photocatalytic water splitting, using solar energy to generate clean hydrogen and oxygen, stands out as a promising clean energy technology. Its potential lies in offering a versatile and clean energy carrier that can be utilized across various sectors, including transportation, industry, and power generation [1].

Methodology / Experimental approach

First, photocatalytically active MOFs [for example UiO-66(Zr), Cu-BDC (Cu), [NH2-MIL-125(Ti)] were synthesized using a solvothermal method. The synthesis process involves combining the metal ions/clusters with organic linkers in a DMF/MeOH mixture under controlled conditions (temperature, pressure, reaction time)[2]. This promotes the formation of crystalline MOF structures with predefined pore sizes and surface properties.

Next, Ni-doped Cu-BDC and [NH2-MIL-125(Ti)] were combined in a controlled manner to form the heterojunction. This involves the deposition of one MOF (Ni-doped Cu-BDC) onto the surface of the other (NH2-MIL-125(Ti)).

The materials were characterized using various techniques such as FT-IR, SEM, EDAX mapping, XRD, and UV-visible absorption. The production of hydrogen using pure [Cu-BDC/Ni] and [NH2-MIL-125(Ti)] was assessed in terms of their respective photocatalytic efficiencies. Further research was done on the catalytic performance of the associated MOFs heterojunction [3].

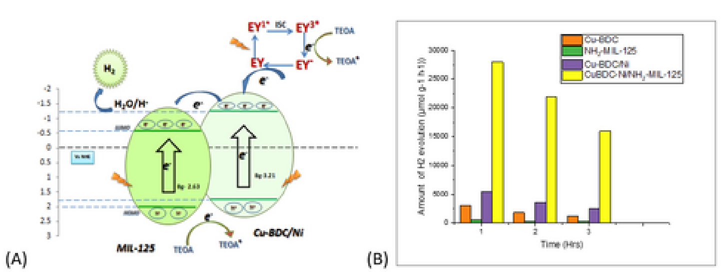


FIG- (A) Schematic representation of a heterojunction with [Cu-BDC/Ni] and [MIL-125-NH2]
(B) Photocatalytic activity of [Cu-BDC], [NH2-MIL-125(Ti)] [CU-BDC/Ni] MOFs and, of the [Cu-BDC/NH2-MIL-125(Ti)] heterojunction.

Objectives and stakes

(i)Designing Novel MOFs photocatalysts by construction of MOF/MOF heterojunctions for increased photocatalytic activity.
(ii) Shaping of MOFs with a binding formulation including a hydraulic binder, followed by a pasting process in the absence of solvent or granulation.
(iii) Introduction of larger mesopores by thermal treatment of partially thermoresponsive MOFs.
(iv) Evaluate the performance of the new materials for photocatalytic water splitting to produce hydrogen under solar light irradiation.

Main results

A solvothermal approach that is dependable, economical, and efficient was utilized to effectively synthesize a range of Cu-based MOFs with defects, functionalization, and doping with Ni2+ions. In order to build MOF-MOF heterojunctions, Zr-based MOF [UiO-66] and Ti-based MOF [NH2-MIL-125(Ti)] have also been developed. By introducing a monocarboxylic acid [4-carboxybenzaldehyde], defects were intentionally introduced into the Cu-BDC MOF. This process resulted in the formation of coordinatively unsaturated metal sites, which can act as active sites crucial for catalytic reactions. Incorporating Ni during the synthesis process led to the creation of doped MOF structures. These enhancements are expected to significantly boost the overall photocatalytic performance of the MOF[4].

We finally combined Ni-doped [Cu-BDC] and [NH2-MIL-125(Ti)] to engineer a heterojunction structure. The resulting heterojunction exhibits synergistic properties which show a remarkable increase in photoproduction of hydrogen. When compared to the individual Cu-BDC/Ni (4000 μmol g-1 h-1) and NH2-MIL-125 (300 μmol g-1 h-1), the resulting [Cubdc-Ni/NH2-MIL-125] exhibits a markedly enhanced photocatalytic activity (28000 μmol g-1 h-1).

References

1 Li J, Huang H, Liu P, et al (2019) Metal-organic framework encapsulated single-atom Pt catalysts for efficient photocatalytic hydrogen evolution. J Catal 375:351–360. https://doi.org/10.1016/j.jcat.2019.06.024
2. Guo C, Wang T, Zhang L, et al (2022) Precise regulation of defect concentration in MOF and its influence on photocatalytic overall water splitting. Nanoscale 14:15316–15326. https://doi.org/10.1039/d2nr03602a
3.Wang Y, Yu Y, Li R, et al (2017) Hydrogen production with ultrahigh efficiency under visible light by graphene well-wrapped UiO-66-NH2 octahedrons. J Mater Chem A Mater 5:20136–20140. https://doi.org/10.1039/c7ta06341e
4. Peng Z, Abbas SC, Lv J, et al (2019) Mixed-metal organic framework-coated ZnO nanowires array for efficient photoelectrochemical water oxidation. Int J Hydrogen Energy 44:2446–2453. https://doi.org/10.1016/j.ijhydene.2018.12.064

Optimization of a Novel Additive Manufacturing Process for Food Production

By Juan-David ORTIZ, 1st year

Supervisors: Graciela CARES, Véronique FALK, Julien KISTNER

Keywords 3D printing · Food processing · Freeform · Food powder · Wheat flour · Starch

PRODUCT ENGINEERING, LA PÂTISSERIE NUMÉRIQUE

General context, scientific issue

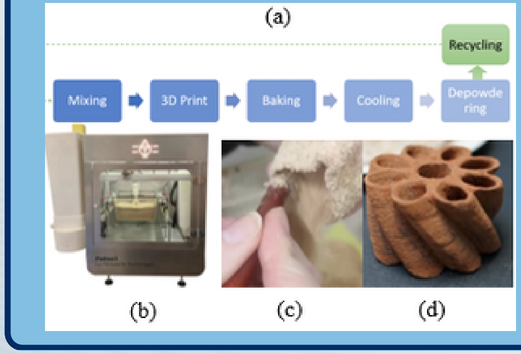
This thesis, a collaboration between the LRGP and La Pâtisserie Numérique, aims to understand the challenges of additive manufacturing of food products using novel FF AM technique. The objectives are:
- to improve FF technique for food production by studying chemical, physical and physicochemical properties of food materials.
- to understand the link between the properties of the 3D-printed pieces, the materials properties, and the process parameters.
- to define key properties for formulating new paste and powder recipes.

Methodology / Experimental approach

One of the focuses is on studying the properties of the materials used for 3D food printing. This includes examining the chemical, physical, and physicochemical properties of the powder and binder, as well as their interactions. Physical characterization of the powder includes particle properties (particle size distribution, true density) and bulk properties (compacity, flow properties[VF1]). Special attention is given to food properties in cereals (starch gelatinization) and recyclability of powder matrix

The focus will shift to the fabrication of 3D-printed food structures, relating the properties of the produced biscuits, with powder properties and process parameter s. Experimental designs will be implemented to identify key factors that impact the quality of 3D-printed biscuits.

Finaly, based on the previous findings, a new food powder formulation will be tested to validate key properties that allow for the improvement of the FF technique



AM process for food production (a), 3D Food printer (b), depowdering step (c) and biscuit (d).

Objectives and stakes

This thesis, a collaboration between the LRGP and La Pâtisserie Numérique, aims to understand the challenges of additive manufacturing of food products using novel FF AM technique. The objectives are:
- to improve FF technique for food production by studying chemical, physical and physicochemical properties of food materials.
- to understand the link between the properties of the 3D-printed pieces, the materials properties, and the process parameters.
- to define key properties for formulating new paste and powder recipes.

Main results

The rheological behavior of the binder impacts 3D printin g process and needs to be well-controlled. Interaction between the binder and powder occurs on the surface which exhibits low wettability at room temperature during 3D print step. Baking step allow physicochemical transformation of powder and binder into the final biscuit. Starch gelatinization is suspected to play a role in layer-by-layer adhesion. Additionally, the amount of starch available to gelatinize decreases with the number of processing cycles.

The expected results from this thesis include a comprehensive understanding of the materials and processes conditions necessary for 3D food printing allowing the adaption of new techniques to the food industry.

References

[1] F. C. Godoi, B. R. Bhandari, S. Prakash, and M. Zhang, "An Introduction to the Principles of 3D Food Printing," in Fundamentals of 3D Food Printing and Applications, Elsevier, 2019, pp. 1–18. doi: 10.1016/B978-0-12-814564-7.00001.

[2] S. Zhu, P. Vazquez Ramos, O. R. Heckert, M. Stieger, A. J. van der Goot, and M. Schutyser, "Creating protein-rich snack foods using binder jet 3D printing," J Food Eng, vol. 332, Nov. 2022, doi: 10.1016/j.jfoodeng.2022.111124.

[3] S. Chen et al., "Freeform 3D printing of soft matters: recent advances in technology for biomedical engineering," Biomedical Engineering Letters, vol. 10, no. 4. Springer Verlag, pp. 453–479, Nov. 01, 2020. doi : 10.1007/s13534-020-00171-8.

Coupling AI and molecular modeling tools for fast and reliable chemical product design

Maria Prokopidou, 1st year
Supervisors: Dimitrios Meimaroglou, Olivier Herbinet

Keywords Modeling tools · Machine learning · Molecular modeling · Monte Carlo methods · Statistical analysis of data · Thermodynamic properties of molecules

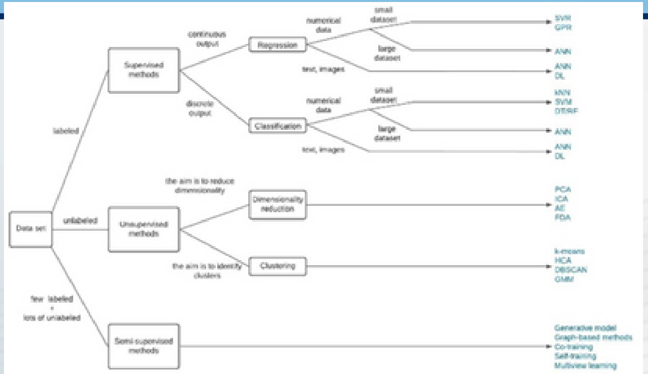
PRODUCT ENGINEERING

General context, scientific issue

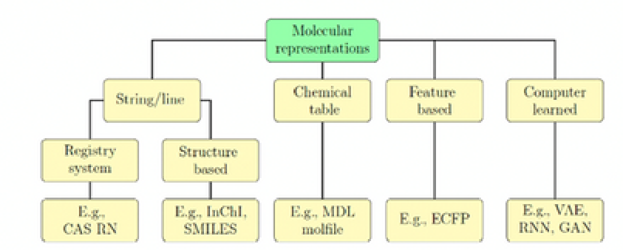
The accurate modeling of thermodynamic and kinetic properties of mixtures requires knowledge of thermochemical and thermophysical molecular properties. However, experimental data of pure molecules are not always available for numerous species of interest and, in certain cases, some properties of molecules in their pure form cannot even be measured in practice. The development of computational tools enabling the prediction of such properties is thus a pivotal requirement for the characterization of these products and for the further development of innovative solutions in different scientific areas, such as the areas of product engineering, energy, chemical reaction kinetics and retrosynthesis, process simulation, catalyst design, drug discovery, and, in general, computer-aided molecular design (CAMD). Today, Group-Contribution (GC) methods, Quantum Chemistry (QC) and Monte Carlo (MC) simulations are used for the prediction of these properties, but their reliability is often subject to question, especially when it comes to newly developed molecules.

Methodology / Experimental approach

Building on a previous PhD, the different techniques of molecular representation will be analyzed and compared in terms of their advantages and drawbacks, to be used as input to different ML techniques. The overall objective is to develop a model that is capable of decoding and using all the necessary input features that allow distinguishing the thermodynamic properties of different molecules, without feeding the model with too much redundant data.
Once the most suitable molecular representation technique is identified, different supervised learning techniques will be employed to calculate different properties of interest.



General guidelines for choosing appropriate ML methods [1].



Different classes of molecular representations [2].

Objectives and stakes

In this research, a coupling of QC, MC and ML techniques is proposed in order to build a powerful predictive tool for the determination of thermochemical (e.g., enthalpy and entropy of formation) and thermophysical (critical temperature, critical pressure, acentric factor and the specific heat capacity) properties of different classes of molecules. The automatization of the calculation of QC properties as well as the postprocessing of its outputs will also be part of the objectives of the thesis. In addition, the use of graphical methods, such as Graph Neural-Networks (GNN) will be investigated as alternative to the use of molecular descriptors, for a more robust representation of the molecules and control of the desired molecular characteristics that need to be considered as inputs to the model. Finally, the developed models will be benchmarked, whenever possible, against GC and MC results and will be further employed in applications for which the implementation of the latter is constrained or infeasible.

Main results

Being only on the 3rd month of the PhD, no results have been produced yet. The above figures are taken from the results established by the preceding PhD on this study and concern the use of molecular descriptors for the prediction of the enthalpy of formation and the entropy of molecules.
A review report on the current state-of-the-art of molecular representation approaches for similar studies is currently under preparation.

References

[1] Trinh C. et al., Processes 2021, 9(8) :1456.
[2] Wigh D.S. et al., WIREs Comput. Mol. Sci., 2022, 12(5) :1603.
[3] Trinh C. et al., Processes, 2023, 11 :3325.
[4] Trinh C. et al., Algorithms, 2023, 16 :573.

Advanced printable composites from MDF waste to furniture

Johan Ramaux, 3rd year
Supervisors: Cécile Nouvel, Isabelle Ziegler-Devin
Arnaud Besserer

Keywords 3D printing · Medium density fireboard (MDF) · Wood composite · Recycling · Thermoplastic

PRODUCT ENGINEERING, LERMAB, ACTA MOBILIER

General context, scientific issue

Wood-derived products, in particular medium-density fiberboard (
economical and mechanical performances. However, in Europe, only 30
products are recycled [1]. To meet this challenge, Acta Mobilier (Yonne
unique new products using 3D printable formulation based on MDF wast

Methodology / Experimental approach

1/ Multi-modal characterization of the (PLA) and the MDF sawdust. The
tightly correlated to the MDF suppliers and machining activities…

2/ Feasibility of the composite formulation, of its 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 Fused Granular Fabrication (FGF).

Graphical abstract of the project

Objectives and stakes

The general overall objective of this thesis is the production of a printable biosourced composite including both MDF sawdust as a reinforcement and poly(lactic acid) (PLA) as a matrix. 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 Mobilier (cf. figure).

Main results

After successfully characterization of the PLA matrix and MDF sawdust by different methods (infrared spectroscopy, microscopy), different formulations (with 20 wt.% MDF and different compatibilizers) were produced on a twin-screw extruder. The resulting composite was characterized in several respects, with the aim of understanding its behavior. The Melt Flow Index was measured, revealing an increase in the material's fluidity when MDF fibers were added. This increase exceeds the literature data for materials used in filament 3D printing, which are around 10 g/10min [2] (180°C / 2.16kg). In addition, Steric Exclusion Chromatography analysis shows polymer degradation during the mixing process. Finally, 3D printing of composites with the FGF process enables us to correlate composite characterizations with the results obtained in 3D printing. Up to date, measurements are still required to complete our understanding of the material evolution during the printing process. To improve the final properties of the composite, the addition of a compatibilizer [3] and the hydrothermal pretreatment of sawdust are currently under investigation.

References

[1] BESSERER Arnaud, TROILO Sarah, GIRODS Pierre, ROGAUME Yann and BROSSE Nicolas. Cascading Recycling of Wood Waste: A Review. Polymers. 27 May 2021. Vol. 13, p. 1–14. DOI: 10.3390/polym13111752.
[2] WANG Sisi. Can the melt flow index be used to predict the success of fused deposition modelling of commercial poly(lactic acid) filaments into 3D printed materials? Plastics Rubber and composites. November 2017. Vol. 47, p. 9–16. DOI: 10.1080/14658011.2017.1397308.
[3] CHANSODA K, SUWANJAMRAT C and CHOOKAEW W. Study on processability and mechanical properties of parawood-powder filled PLA for 3D printing material. IOP Conference Series: Materials Science and Engineering. 1 February 2020. Vol. 773, p. 1–4. DOI: 10.1088/1757-899X/773/1/012053.

Development of a lithium carbonate precipitation process for the recycling of Li-ion batteries

By Lorena Ramírez, 2nd year

Supervisors: Hervé Muhr, Ludivine Franck-Lacaze

Keywords Circularity Hydrometallurgy Precipitation Li-ion batteries Lithium recovery Carbonation

PRODUCT ENGINEERING, EMMAD

General context, scientific issue

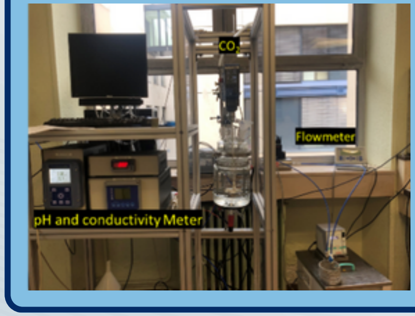
Lithium-ion battery waste is increasing at a rate of 20 percent annually, projected to exceed 136,000 tons by 2036. Improper disposal poses environmental, health and safety risks alongside legal and economic implications. The battery recycling industry is burgeoning due to regulatory mandates, environmental awareness, and raw material shortages. Prioritizing battery recycling is critical to mitigate these challenges and ensure a sustainable supply of materials for energy storage. [1].

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 / Experimental approach

Lithium carbonate was obtained by addition of Na2CO3 (liquid-liquid precipitation) and by using CO2 (gas-liquid precipitation). Experiments were performed in a jacketed semi-batch reactor, which was thermostatically controlled and stirred system. Experimental conditions were varied, to make a quantitative and qualitative analysis of the final product obtained by both methodologies. 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).



Photograph of the experimental set-up for the gas-liquid precipitation approach.

Main results

The different operating conditions tested in this study have a significant impact on both the morphology and lithium content of Li2CO3 precipitate. Figure 1 shows the relationship between the morphology of solids obtained with L-L and G-L precipitation and the mean particle size. Both methologies exhibit a spherulitic growth, however smaller particles are formed when using Na2CO3. Aditionally, higher gas flow rates lead to the formation of larger particles.

Figure 2a shows the results of recovery yield and purity of the solids obtained using Na2CO3 where is observed an improvement of yield with higher lithium concentrations in the feed solution. In figure 2b, both methodolgies demonstrate standard recovery yields, however employing CO2 at 8 L/min results in superior purity levels.

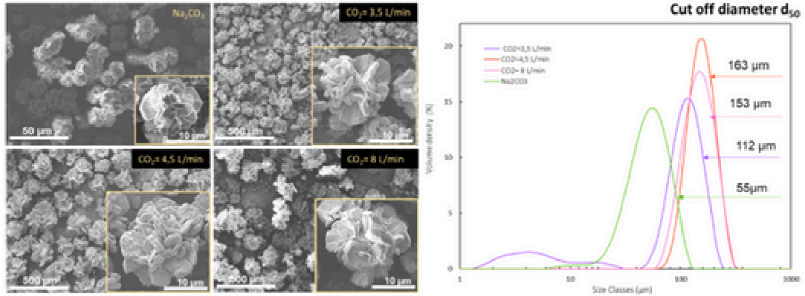


Figure 1. Scanning electro images and particle size distribution curves from the solids obtained through liquid-liquid and gas-liquid orecipitation, corresponding to flow rates of 3,5, 4,5 and 8 L/min.

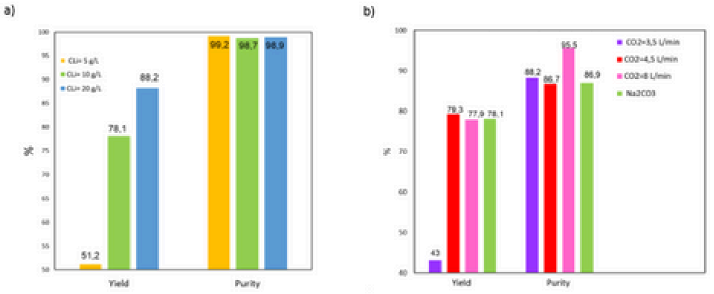


Figure 2. a) Purity and lithium recovery results of the L-L preciptation at different lithium concentrations of the feed solutions b) Purity and recovery yield from the solids obtained through liquid-liquid and gas-liquid precipitation.

References

[1] McKinsey & Company (March 13,2023) Battery recycling takes the driver's seat https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-recycling-takes-the-drivers-seat# (consulted on May 2024).

Modelling of rheologically evolving fluids

By Adilson SAMBA, 3rd year
Supervisors: Cécile LEMAITRE, Philippe MARCHAL

Keywords Time-dependent fluids | Thixotropy | Viscoelasticity | Reactive fluids | Yield-stress fluids | Structural modeling | Numerical simulation

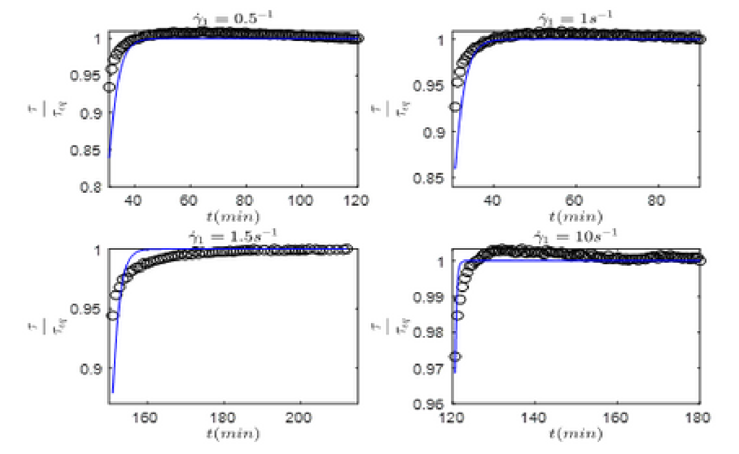
PRODUCT ENGINEERING

General context, scientific issue

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, destructuration occurs leading to facilitated flow of the fluid and therefore to a lower viscosity. This destructuration 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.

Methodology / Experimental approach

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 LRPG (a stress-controlled rheometer ARG2 and a strain-controlled rheometer ARES, both from TA Instruments).



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.

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.

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:

$$\begin{cases} \eta(\dot\gamma) = k(\lambda)\dot\gamma^{n-1} + \dfrac{\tau_y}{\dot\gamma} \quad if \;\; \dot\gamma \geq \dot\gamma_c \\ \eta(\dot\gamma) = \dfrac{\tau_y}{\dot\gamma_c}\left(2 - \dfrac{\dot\gamma}{\dot\gamma_c}\right) + k(\lambda)\dot\gamma_c^{n-1}\left((2-n) + (n-1)\dfrac{\dot\gamma}{\dot\gamma_c}\right) \quad if \;\; \dot\gamma < \dot\gamma_c \end{cases} \tag{1}$$

where λ is governed by Moore kinetics:

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

References

University of Prague, 1981.
Mewis, Jan, and Norman J Wagner. "Thixotropy." Advance in Colloid and Intrface Science, 2009: 214–227.

Recycling in short circuit of used plastic mixtures by additive manufacturing

By Benjamin Sandei, 2nd year

Supervisors: Cécile Nouvel, Valérie Massardier

Keywords Polymer blend Extrusion Additive manufacturing Recycling Post-consumer plastic Circular economy

PRODUCT ENGINEERING, IMP

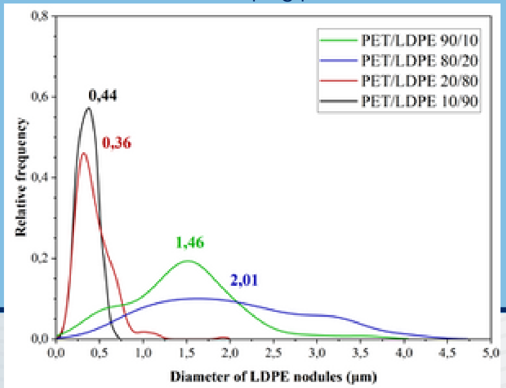
General context, scientific issue

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 hard 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].

Methodology / Experimental approach

After selecting the mixtures to be studied, the first objective of this work will consist in compatibilizing virgin polymers representative of these streams, with the aim to design "model" blends formulated and 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 equipments 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.



Size distribution of LDPE nodules in the PET/LDPE blends with different relative mass ratio

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" through a collaboration between LRGP and IMP with ERPI and Centrale-Supélec. More specifically, this concerns the short-circuit valorization of post-consumer polymer wastes that are 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.

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 in PET streams look to be the most common issue encountered during mechanical recycling. Then, a bibliographic approach has been carried out regarding the miscibility of PE and PET. 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 was first performed on virgin PET and PE, representing plastic waste. Rheological analysis has shown a very important difference in their viscosity, and some thermal mechanical degradation under air, which constitute major challenges to produce blends [3]. Then, PET/PE blends have been made, with ratio of PE corresponding to the ones used on packaging industry. As the PE acts as a default on the PET, it induces a decrease in the mechanical properties of the PET. Thus, blends with additional PE have been realized and characterized. It seems that the use of PET as a reinforcement of PE matrix represent a more interesting way of valorization for polymer trays. The study of the compatibilization of these blends and their printability is the next step of this thesis, before trying to extrapolate the formulation to polymer waste.

References

[1] Mikula K. et al., Environ. Sci. Pollut. Res. 2021. 28 :12321-12333
[2] Ihm D. et al., J. Appl. Polym. Sci. 1996. 60:1-7
[3] Chen S. et al.,Polymers. 2018. 10:147-160

Synthesis of quaternary quantum dots for photovoltaic applications

By Shubham Shishodia, 2nd year
Supervisors: Raphaël Schneider, Thomas Gries

Keywords Quantum dots · Aquaeous synthesis · Surface functionalization · Optoelectronic properties · Photoanodes · Photovoltaics

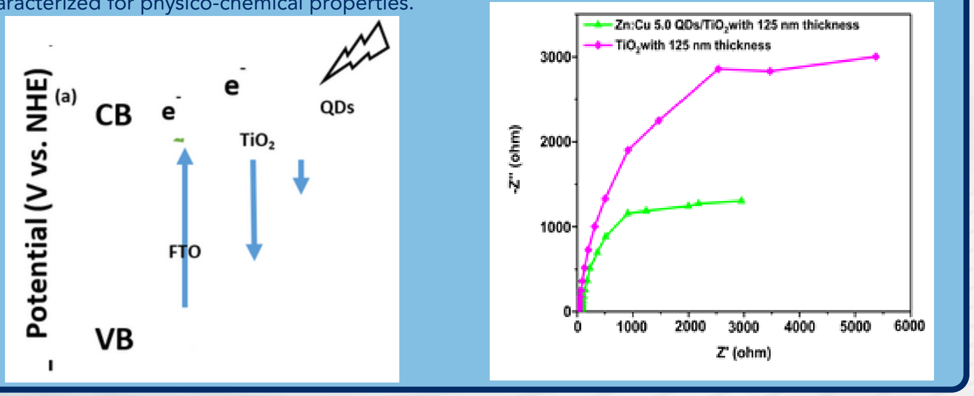
PRODUCT ENGINEERING

General context, scientific issue

Ever growing energy needs and the associated detrimental consequences pose significant challenges to the mankind. It becomes imperative to work towards developing alternative, 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]. After integration into solar cells, QDs can be used as effective solar spectrum absorbers. Their tunable bandgap in accordance with the energy level, makes them an attractive solution for multi-junction solar cells [2][3].

Methodology / Experimental approach

The microwave-assisted aqueous phase-based synthesis of Cu-In-Zn-Se/ZnS QDs was performed by using In, Cu, Zn, and Se precursors, and a surface ligand. The prepared solutions were microwaved in short pulses. The synthesis protocol was optimized by considering various factors, such as molar ratios of Cu:In:Zn:Se, selection of surface ligands and pH. 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. Then, a crack-free layer of QDs on TiO2 photoanode was prepared to prevent any charge recombination and hinder electron transport within the QDs/TiO2/FTO heterostructure. The fabricated QDs/TiO2 photoanodes were characterized for physico-chemical properties.



a) The proposed energy band structure and (b) EIS curves used to investigate the charge transfer in assembled QDs/TiO2/FTO heterostructure.

Objectives and stakes

The objectives of the undertaken study are:
·Synthesis of environmentally benign, Cd-free Quantum dots (QDs) by developing robust aqueous solution-based techniques.
·Characterization of synthesized QDs to understand their optical, structural and electrical properties.
·Preparation of TiO2 photoanodes by DC magnetron sputtering and deposition of QDs on prepared TiO2 photoanodes by suitable coating technique.
·Characterization of QDs-sensitized TiO2 photoanodes by photoelectrochemical studies to understand the charge transport and recombination processes.

Main results

The Cu-In-Zn-Se/ZnS QDs synthesized by microwave-assisted aqueous phase-based approach possess tunable energy band gap from 1.73 to 2.12 eV by control of their non-stoichiometry and their PL can be tuned from 618 to 765 nm. The QDs having a Zn:Cu molar ratio of 0.5 exhibit the longest mean decay PL lifetime of 0.63 μs with the highest PL QY of 54%.Dip coating of Cu-In-Zn-Se/ZnS QDs on the magnetron sputtered TiO2/FTO substrate resulted in the fabrication of QDs-sensitized electrode. Techniques like SEM, TEM, EDX and DRS were extensively employed to monitor the coating on the surface of the fabricated electrode. Photoelectrochemical measurements on tailored QDs-sensitized electrode were conducted. Improved steady-state current response and dynamic response of the heterostructured QDs/TiO2/FTO films to intermittent illumination was recorded by chopped light chronoamperometry. Mott-Schottky analysis revealed the n-type doping behaviour of the QDs and energy band alignment suitable for electron transfer within the QDs/TiO2/FTO heterostructure by virtue of flat-band potential measurements. The presence of a small and tight semi-circular shape in Nyquist plot in comparison to unsensitized TiO2 film electrode indicated an improved charge transfer with minimal interfacial effects. The study demonstrates high application prospect of Cu-In-Zn-Se/ZnS QDs sensitized TiO2 thin film electrodes in QDs-sensitized solar cells.

References

[1] Bera, D.; Qian, L.; Tseng, T.K.; Holloway, P.H. Quantum dots and their multimodal applications: A Review. Materials 2010, 3, 2260–2345.
[2] García de Arquer, F.P.; Talapin, D.V.; Klimov, V.I.; Arakawa, Y.; Bayer, M.; Sargent, E.H. Semiconductor quantum dots: Technological progress and future challenges. Science 2021, 373, eaaz8541.
[3] Shishodia, S.; Chouchene, B.; Gries, T.; Schneider, R. Selected I-III-VI2 Semiconductors: Synthesis, Properties and Applications in Photovoltaic Cells. Nanomaterials 2023, 13, 2889.

Processing of mixed plastic waste for distributed large-scale 3D printing

By Catalina Suescun Gonzalez, 3th year

Supervisors: Hakim Boudaoud, Cécile Nouvel, Joshua Pearce

Keywords 3D printing · Multi-material · Plastic blend · Recycling · Waste-based · Fused Granular Fabrication · Distributed

PRODUCT ENGINEERING, ERPI, FAST

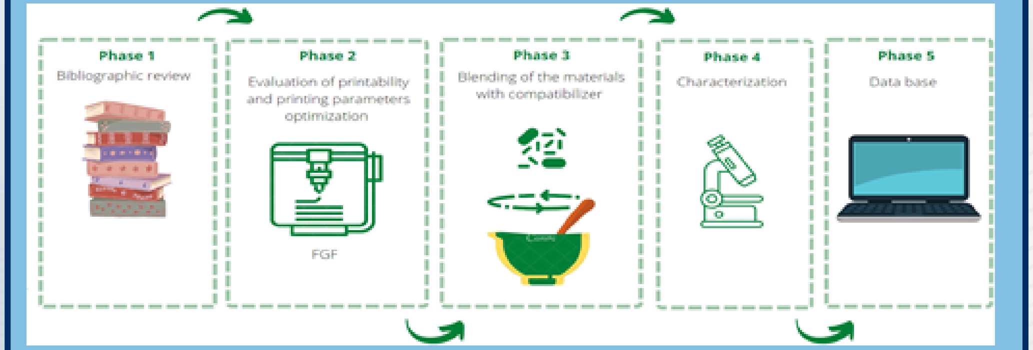
General context, scientific issue

This thesis, a collaboration between the LRGP and La Pâtisserie Numérique, aims to understand the challenges of additive manufacturing of food products using novel FF AM technique. The objectives are:

- to improve FF technique for food production by studying chemical, physical and physicochemical properties of food materials.
- to understand the link between the properties of the 3D-printed pieces, the materials properties, and the process parameters.
- to define key properties for formulating new paste and powder recipes.

Methodology / Experimental approach

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 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 that 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. As a study model an example of potential distributed recycling, we considered here a common waste product, a Cristalline© brand water bottle.



Thesis Methodology

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 objectives. Firstly, study the feasibility of direct printing multi-material recycled 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, assessment of the reproducibility and transferability of the model to other countries , through a comparison of European and North American systems.

Main results

At first, a systematic literature review was 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 with relatively inexpensive equipment that can easily be installed in a “fablab” or similar facility: 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 have 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 [5]. Secondly, the use of three compatibilizers, both reactive and non-reactive, have been tested to improve material properties and facilitate printing, and injected samples have been produced for comparison.

References

[1] Godswill, A et al. Impacts of Plastic Pollution on the Sustainability of Seafood Value Chain and Human Health. 5, 93 (2019).
[2] Pavlo, S et al. 3D-Printing Based Distributed Plastic Recycling: A Conceptual Model for Closed-Loop Supply Chain Design in 2018.
[3] Zhong, S et al. Tightening the loop on the circular economy: Coupled distributed recycling and manufacturing with recyclebot and RepRap 3-D printing. Resources, Conservation and Recycling 128, 48–58 (2018).
[4] Woern, A. et al. Fused Particle Fabrication 3-D Printing: Recycled Materials’ Optimization and Mechanical Properties. Materials 11, 1413 (2018).
[5] Suescun Gonzalez, C et al. Multi-material distributed recycling via material extrusion: recycled high-density polyethylene and poly (ethylene terephthalate) mixture. Polymer Engineering & Science (2024)

Comprehension of process parameters' impact on solid/liquid extraction of sinapic acid and sinapine from rapeseed meal

By Apolline Tollitte (research engineer)
Supervisors: Romain Kapel, Sara Albe-Slabi

Keywords Solid/liquid extraction · Phenolic compounds · Sinapic acid · Sinapine · Rapeseed

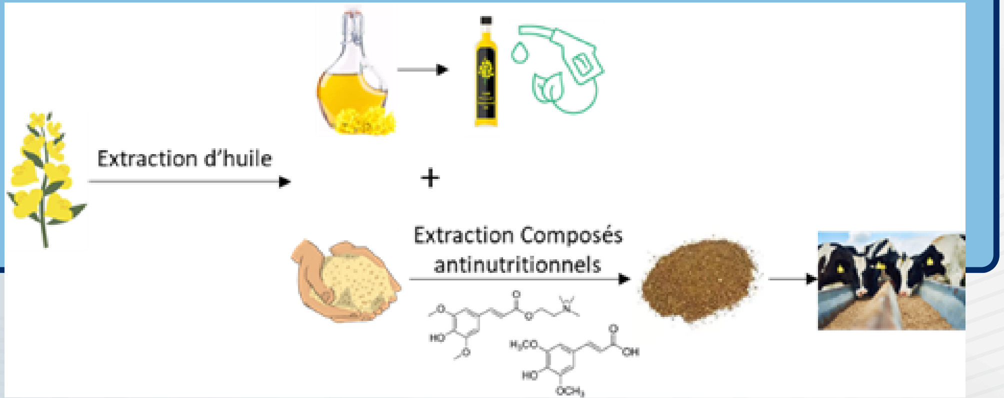
PRODUCT ENGINEERING, PROCEED

General context, scientific issue

Nowadays, rapeseed is one of the most grown oilseed crops, with a production exceeding 70 million tons per year [1]. Currently, it is exploited for its oil, which represents between 40 and 50% of the dry matter of the seed. Then, this oil is consumed in the production of biofuels or in food industry. On the other hand, the meal, which is a solid by-product from oil extraction, is used in animal feed as a source of fiber and protein.

Methodology / Experimental approach

As a first step, COSMO-RS model was used to predict the thermodynamic behavior of the solvent-solute system of sinapic acid (SA) and sinapine (SN). This approach handles the interactions between molecules in liquid solutions starting from the surface charge distribution of molecules ideally screened to achieve the prediction of thermodynamic properties for a given system [3]. More specifically, COSMO-RS model helped to determine the solubility of SA and SN in various solvents at temperatures between 20 and 60°C. Then, the modelized results were compared to an experimental approach and a series of solid/liquid extractions from rapeseed meal was performed by varying the solvent composition (concentration of ethanol:0, 20, 40, 60, 80 and 100%) and temperatures (20, 40, 60 and 80°C).



General scheme for the recovery of rapeseed meal

Objectives and stakes

However, rapeseed meal contains anti-nutritional compounds that can decrease its quality. Among them, phenolic compounds such as sinapic acid and its derivatives, like sinapine, may be associated with bitter taste that affects food intake [2]. The aim of the present investigation was to enhance the understanding of the extraction systems of phenolic compounds (PC), sinapic acid (SA) and sinapine (SN) from rapeseed meal.

Main results

On one hand, the COSMO-RS model highlighted that SA had very low affinity with water. Also, water/ethanol solutions seemed to be more efficient to solubilize SA than pure water, especially at high temperature. On the contrary, SN was more soluble in water than in alcohols or acetone and acetonitrile. On the other hand, the various extractions made showed that SA and SN were best extracted in aqueous solvents (20-80% ethanol). In addition, extraction of the PC in pure water was more efficient at the different studied temperatures. On the contrary, a reduction of the PC's extraction efficiency was observed in pure ethanol. This reduced performance of ethanol could indicate a deeper affinity between the solid phase and the liquid phase, limiting the impregnation of the solid by the solvent. Ethanol would have access to a lower surface compared to aqueous solvents and therefore would solubilize less PC. Another intriguing point was the rate of SA and SN in the total rate of PC, representing respectively 10% and 45% under most of the conditions studied. However, an unusual behavior was observed in pure ethanol: extraction of SN was minimal (about 20%) unlike extraction of SA reached a maximum (about 15%). This could suggest the use of pure ethanol would improve selectivity towards SA. Finally, the temperature did not seem to show any impact on extraction yields, except in the case of pure ethanol where an increase in extraction yield was observed with the increase in temperature.

References

[1] Food and Agriculture Organization of the United Nations, 2023
[2] Matthäus, B., & Angelini, L. G. (2005). Anti-nutritive constituents in oilseed crops from Italy. Industrial Crops and Products, 21(1), 89–99
[3] Klamt, A. (1995). Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena. The Journal of Physical Chemistry, 99(7), 2224–2235

Fick’s second law of diffusion:
Examining mathematical approximations and their potential for associated misinterpretations

By Pan Wang, 4th year
Supervisors: Guo-Hua Hu, Sandrine Hoppe

Keywords Fick's second law | Diffusion coefficient | Analytical solutions | Numerical approaches

PRODUCT ENGINEERING

General context, scientific issue

Fick's second law is commonly used to describe the diffusion of molecules from one spatial region to another and is defined by a diffusion coefficient, denoted as D. In many cases, it can be mathematically represented as an infinite series [1]. However, determining D analytically in such cases becomes impractical, necessitating numerical approaches. Historically, the computational demands for numerical solutions were challenging. Consequently, analytical solutions emerged as a historical approximation for the infinite series of Fick's second law, particularly for short-time diffusion processes. Nevertheless, these analytical solutions inherently possess two limitations: (i) they rely solely on experimental data from the initial stages of diffusion processes to calculate D, neglecting data closer to the later stages of diffusion processes; (ii) they may lead to a misinterpretation of Fick's second law. Indeed, many publications argue that if experimental data align with an analytical solution, the diffusion process adheres to Fick's second law. Conversely, if the data deviate, the diffusion process is considered not to follow Fick's second law [2].

Methodology / Experimental approach

(i) Theoretical analysis: An infinite series with integer n from zero to infinity is employed in Fick's laws of diffusion. To determine D, a specific n must be chosen. Higher n increases accuracy but also computation time. The absolute error, AE(n), quantifies accuracy and depends on slab thickness (L), D, and diffusion time (t).

(ii) Comparative analysis: The accuracy and applicability of two typical mathematical approximations of Fick's second law, which are frequently used due to their simplicity, are evaluated based on the magnitude of the ratio M(t)/M∞. The turning point, M(t)/M∞ = 0.6, is analyzed through derivative and error analysis methods. Relative error (RE) is used to compare the accuracy for the approximate equations with the finite equation of Fick’s second law obtained in section (i) at each specific M(t)/M∞.

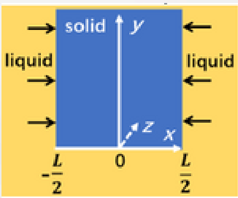
(iii) Experimental data application: Validation of the accuracy of the diffusion coefficient calculation using experimental data from the literature. The scaled error (qi) is introduced to achieve independence from the scale of the data [3].

References

[1] A. Fick*. On liquid diffusion. 1855, 10: 30–39.
[2] O. Menezes and K. Davami* et al., Polym. Degrad. Stabil. 2022, 199: 109903.
[3] R. Hyndman and A. Koehler*. Int. J. Forecasting 2006, 679–688.
[4] R. Pantani*and F. Santis et al., Polymer 2016, 99: 130–139.

Objectives and stakes

The objectives of this study are dual: (i) To replace analytical solutions of Fick's second law with a computational approach to determine D. Unlike the historically proposed analytical solutions, which are limited to the early stage of a diffusion process, the computational approach allows the utilization of experimental data throughout the entire diffusion process. Furthermore, this computational method can be readily implemented today, even extending to one or two decades ago. (ii) To demonstrate that, even if experimental data diverge from an analytical solution of Fick's second law, they may still align with Fick's second law.



$$\frac{M(t)}{M_\infty}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2\left(\frac{Dt}{L^2}\right)\right]$$

Where *M(t)* is the mass of the liquid diffused into the slab, *M∞* is the total mass of the liquid diffused into the slab at equilibrium.

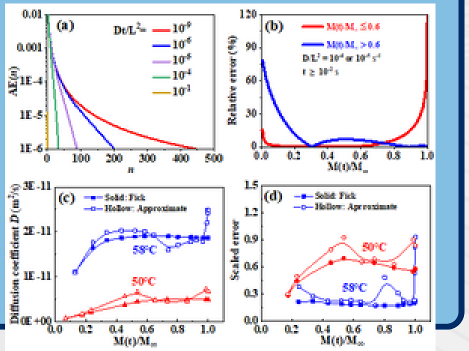
Diffusion of a liquid into a solid slab of thickness L from two sides.

Main results

(i) Figure (a) shows AE(n) decreases with increasing n. Additionally, as the value of Dt/L2 decreases, a higher n is necessary to attain the same AE(n). For instance, when Dt/L2 equals 1 × 10-9, AE(n) reaches 10-6 at n = 447. This underscores that the calculation of D by above equation in illustration, utilizing n = 1000, is reliably accurate, provided Dt/L2 is equal to or greater than 1 × 10-9.

(ii) As shown in Figure (b), the relative error of the value of M(t)/M∞ calculated by the approximate equations compared to Fick’s second law with a finite n=1000, as a function of M(t)/M∞, determines the validity and applicability of the approximate equations at different stages of diffusion process.

(iii) Derived from literature data [4] in liquid water diffusion in amorphous PLA under 50 °C and/or 58 °C, Figure (c) shows the diffusion coefficients calculated by Fick’s second law and approximate equations as a function of M(t)/M∞. The scaled error, as shown in Figure (d), also indicates stable accuracy. The computational approach to determine D effectively replaces the analytical solutions of Fick's second law, allowing the utilization of experimental data throughout the entire diffusion process.



Fundamental Understanding and Application of Epoxidized Natural Rubber Composites

By Zixuan Wang, 2nd year

Supervisors: Guo-Hua Hu, Liqun Zhang

Keywords Epoxidized natural rubber | Strain induced crystallization | Mechanical properties

PRODUCT ENGINEERING

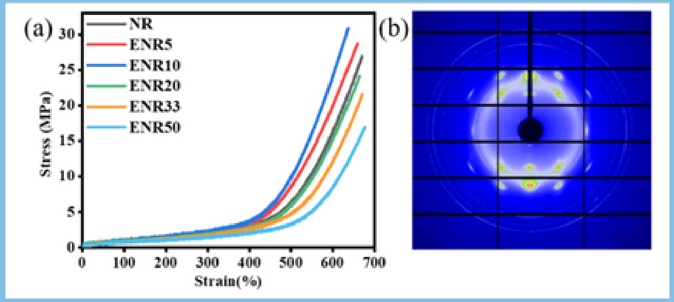
General context, scientific issue

The outstanding mechanical properties of epoxidized natural rubber (ENR) stem from its distinctive strain-induced crystallization characteristic originating from NR[1]. Nevertheless, the influence of epoxy degree on molecular chain orientation, strain-induced crystallization, and the crystallization mechanism of the ENR during the uniaxial tensile process remains undisclosed and requires quantification.

Methodology / Experimental approach

1.Synthesis of ENR via in-situ epoxidation reaction: NR latex with a dry rubber content of 61% and OP-10 surfactant (2% by weight of NR latex) were introduced into a three-necked flask and diluted to 30% by adding distilled water[2]. After 30 minutes of stirring at 40°C, formic acid and hydrogen peroxide were sequentially added following the molar ratio: NR: hydrogen peroxide: formic acid = 1:1:0.55. Following flocculation with ethanol, the ENR was immersed in a 1 wt% sodium carbonate solution for 24 hours and then dried in an oven at 80°C until a constant mass was achieved.

2.Characterization of the chemical structure: The crystal structure of ENR/silica composites was analyzed using Wide-Angle X-ray Diffraction (WAXD), Polarized FTIR, and Atomic Force Microscope (AFM). The relationship between crystallinity, orientation parameters, and stress-strain was determined using the Herman equation, and X-ray data analysis was conducted using Fit 2D software.



(a) Stress-strain curves of NR and ENR; (b) 2D-WAXD diagram of ENR10 under the maximum strain

References

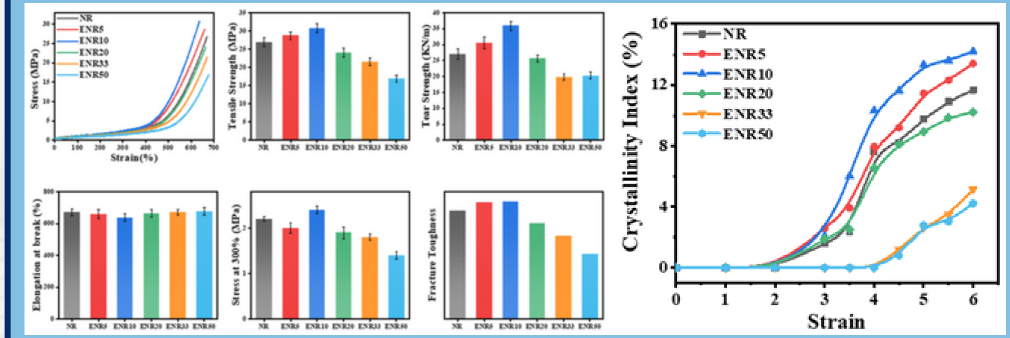
[1] Zhang X. et al., MACROMOL RAPID COMM. 2019, 40:1-5.
[2] Pithaksareetham N. et al., ADV POLYM TECH. 2018, 37:1-12.

Objectives and stakes

ENR samples featuring various epoxy degrees were synthesized through an in-situ epoxidation reaction utilizing NR latex, formic acid, and hydrogen peroxide as raw materials. The impact of epoxy degree on orientation, strain-induced crystallization (SIC), and the crystallization mechanism of ENR was explored employing Wide-Angle X-ray Diffraction (WAXD), polarized infrared spectroscopy (P-FTIR), and Atomic Force Microscopy (AFM).

Main results

NR demonstrates relatively weak mechanical properties, with a tensile strength of 26.9 MPa, tear strength of 27.1 MPa, and a modulus of 2.2 MPa (stress at 300%). It is evident that the incorporation of suitable epoxy groups can significantly enhance the ultimate strength and modulus of ENR. For instance, compared to NR, the tensile strength, tear strength, and modulus of ENR10 reach 30.8 MPa, 35.9 kN/m, and 2.4 MPa, respectively, showing improvements of approximately 14.5%, 32.5%, and 9.1%. However, ENR with a high epoxy degree (ENR33/50) exhibited a decrease in mechanical properties. To gain insight into the mechanism behind the enhancement of ENR, Synchrotron Radiation experiments were conducted.



As the epoxidation degree rises, the material's crystallinity initially increases and then decreases at maximum strain. This suggests that suitable epoxidation can enhance the crystallization of molecular chains, thereby improving mechanical properties. However, higher epoxy degrees can restrict molecular chain movement and orientation, leading to reduced crystallization capacity and deteriorated mechanical properties.

Simulation of the acid hydrolysis of keratin in order to standardize the industrial production of amino acid mixtures, limit its environmental impact and its energy consumption

By Mibé Ibrahim Yeo, 1st year

Supervisors: Romain Kapel, Cécile Lemaitre, Sophie Beaubier, Ghislain Genin

Keywords Agro-resources valorization | Proteins | Keratin | Chemical hydrolysis | Kinetic modelling | Economic and environmental optimization

PRODUCT ENGINEERING, BCF LIFE SCIENCES

General context, scientific issue

Keratin proteins from poultry feathers can be hydrolyzed into multifunctional products like amino acids and peptides. At BCF Life Sciences, keratin hydrolysates processing occurs in a strongly acidic hot aqueous medium for hours, making the process particularly cost- and energy-intensive. Furthermore, the composition of the hydrolysates may vary between batches. As operating conditions currently applied by the manufacturer were established empirically, kinetic modelling and CFD studies would allow further process economic and environmental optimization while enhancing the process stability.

Methodology / Experimental approach

Firstly, a compliant keratin hydrolysate product is defined by the following quality criteria: molar mass distribution of peptides and amino acids, the mass ratio of total peptides to free amino acids, and the concentration of key amino acids (cystine, tyrosine, and phenylalanine). These criteria will be determined experimentally using an adapted analytical method based on Beaubier et al. (2019). Basically, hydrolysate components are separated by SE-HPLC, and post-column UV absorbance provides chromatogram signals convertible into concentrations using the Beer-Lambert law.

Secondly, using the devised analytical method, follow-up of the kinetics of macerates and hydrolysates composition changes will be conducted for a set of experimental conditions reproducing real storage conditions. The durations of the hydrolysis required for reaching the product specifications will be analysed in order to determine the impact of storage conditions on the duration of hydrolysis.

Lastly, for each process stage, kinetic models relating rate constants of key chemical compounds to applied operating conditions (Temperature and/or HCl/keratin ratio) will be developed using a response surface methodology inspired from (Beaubier et al., 2021). These kinetic models will first be used to predict the hydrolysis duration needed to meet product specifications, considering the storage history of the macerate. The kinetic models will then be injected into a genetic-evolutionary algorithm to generate multicriteria Pareto's fronts from which operating conditions minimizing energy and HCl consumption can be identified.

References

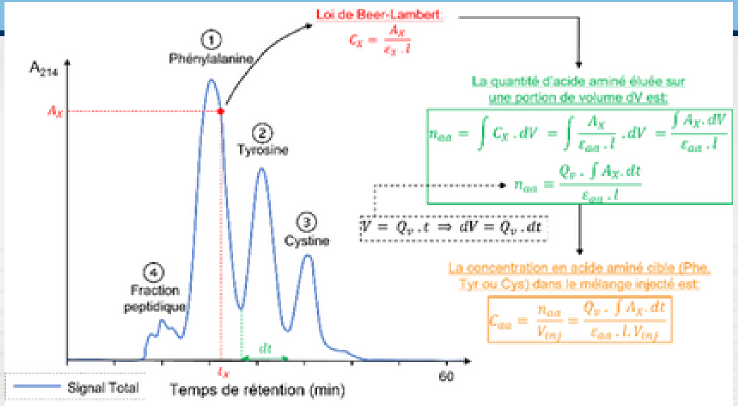
[1] Beaubier et al., 2019. Simultaneous quantification of the degree of hydrolysis, protein conversion rate and mean molar weight of peptides released in the course of enzymatic proteolysis. Journal of Chromatography B, 1105, 1-9.

[2] Beaubier et al., 2021. A new approach for modelling and optimizing batch enzymatic proteolysis. Chemical Engineering Journal, 405, 126871.

Objectives and stakes

The industrial process implemented by BCF Life Sciences involves two stages. The first stage called maceration consists in the controlled acidic solubilization of keratin at 70°C resulting in a keratin-rich mixture or macerate. This macerate is stored for some uneven time in tanks subjected to variable weather conditions wherein partial hydrolysis of keratin started during the first stage is carried on. In the second stage held at about 100°C and upon significant HCl addition, the macerate undergoes nearly complete acid-induced keratynolysis to yield a most compliant keratin hydrolysate mixture in terms of composition. However, unexpected variations in the hydrolysate composition are often observed.

The objective of this work is therefore to develop a tool for simulating the kinetics of changes in the final hydrolysate composition as a function of both the hydrolysis conditions (temperature and HCl/keratin ratio) and the state of the intermediate macerate. This simulation tool will be coupled with a CFD study to create an integrated tool that accurately represents real reactor phenomena while allowing recalculation of optimal hydrolysis conditions for minimizing energy and HCl consumption.



Determination of the concentration of key amino acids using the developed analytical method

Main results

The thesis project started two months ago and the experimental pilot is still under development. No conclusive result is available at the moment.

Synthesis of high molecular weight poly(carbonate-co-ether)s using a dual catalyst of double metal cyanide complex and aluminum porphyrin complex

By Shuo Zeng, 3rd year

Supervisors: Guo-Hua Hu, Liqun Zhang

Keywords CO2 copolymerization | Dual catalyst | Kinetics | Terpolymer

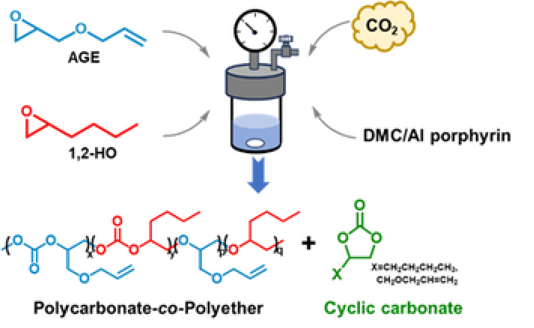
PRODUCT ENGINEERING

General context, scientific issue

The copolymerization of CO2 and epoxides presents a promising strategy for the sustainable development of the polymer industry by utilizing abundant CO2 as a C1 feedstock. Since the discovery of epoxides and CO2 ring-opening copolymerization by Inoue in 1969, various metal complex catalysts have been developed, including salen Co, salen Cr, β-diimide Zn, and metal porphyrins. Among these, aluminum stands out due to its low toxicity, low cost, and abundant availability. Wang et al. synthesized a series of environmentally friendly porphyrin aluminum complexes and evaluated their catalytic properties for the copolymerization of various epoxides and CO2 . However, as the side group length of the epoxide compound increases, the polymer selectivity and molecular weight significantly decrease. The zinc-cobalt(III) double metal cyanide complex (DMC) is a highly efficient catalyst for the ring-opening copolymerization of CO2 and epoxides with long alkyl groups. Our previous studies have shown that under suitable polymerization conditions, the Mn of the polymer exceeds 50,000 g/mol, with the cyclic carbonate by-product kept below 1.0 wt%. However, one disadvantage of this system is its low percentage of CO2 incorporated in the polymer.

Methodology / Experimental approach

In a glove box, DMC, aluminum porphyrin catalyst, and epoxides were charged into a pre-dried high-pressure reactor equipped with a magnetic stirrer. The autoclave was then removed from the glove box and pressurized with 4 MPa CO2 at 60°C. After a specified duration, the autoclave was cooled using an ice-water bath, and the CO2 pressure was gradually released. A small sample of the crude product was extracted for 1H NMR spectroscopy to determine monomer conversion. The remaining products were dissolved in dichloromethane and precipitated with excess methanol to remove unreacted monomers and small molecule by-products. The precipitated polymers were then collected and dried at 35°C under vacuum for 48 hours. A small portion of the purified product was reserved for DSC measurements to determine the Tg.



Schematic diagram of terpolymerizing AGE and HO with CO2 by combinatorial catalyst of DMC and Al porphyrin complex.

Objectives and stakes

This study aims to develop a process for preparing 1,2-hexane oxide (HO)/allyl glycidyl ether (AGE)/CO2 terpolymer poly(carbonate-co-ether)s with high Mn by combining DMC and aluminum porphyrin catalysts. The focus is on investigating the reaction kinetics and the potential mechanism of copolymerization using these dual catalysts.

Main results

The terpolymerization of AGE, HO, and CO2 was conducted using both a single catalyst and a dual catalyst under identical conditions to investigate the impact of the dual catalyst strategy. A polymer with a molecular weight (Mn) of 113 kg/mol was obtained using the dual catalyst at 60 °C. The Mn of the resulting poly(carbonate-co-ether) was notably enhanced by 151% and 310% compared to that catalyzed solely by DMC (45 kg/mol) and porphyrin aluminum (29 kg/mol), respectively. To elucidate the reaction mechanism of the combinatorial catalyst, the apparent reaction kinetics were studied.

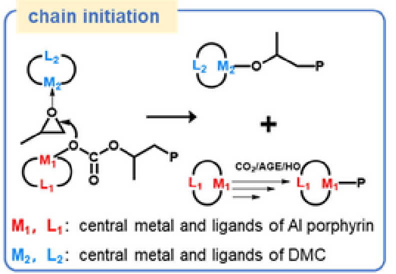


Figure 2. Possible copolymerization mechanism using a dual catalyst

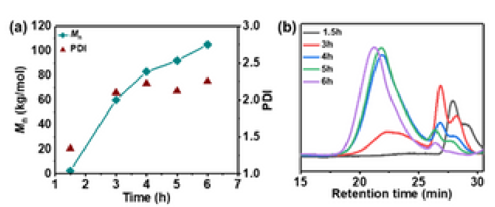


Figure 1. Evolution of the terpolymerization of CO2, AGE, and 1,2-HO. (a) Plots of Mn and PDI versus time, (b) GPC traces of terpolymers at various reaction times.

In Figure 1 (a) and (b), during the initial stage of the reaction (<1.5h), the reaction rate is slow, and the GPC curve exhibits a bimodal distribution, indicating that copolymerization reactions were initiated by Al porphyrin. As the reaction time extends (>1.5h), the reaction rate increases due to the co-participation of DMC and Al porphyrin in the chain growth reaction, resulting in a GPC curve displaying a three-peak distribution. While the exact nature of the active substance of the heterogeneous catalyst remains unknown, a proposed bimetallic mechanism involves the cooperation of two metal atoms (see Figure 2): one binds to the nucleophilic chain end while the other provides coordination for the epoxides to be activated by a nucleophilic attack.

References

[1] Pescarmona P. P. et al., Green Chem., 2023, 25,7612.
[2] Coulembier O. et al., ChemSusChem, 2020, 13, 469–487.
[3] Cao H. et al., SusMat., 2021, 1, 88-104.
[4] Wang X. H. et al., Macromol. Chem. Phys. 2022, 223, 2100403.

Film formation and transition on a partially wetting cylinder upon withdrawal from a Newtonian fluid

By Heng-Kuan Zhang, 2nd year

Supervisors: Cécile Lemaitre, Guo-Hua Hu , Xian-Ming Zhang

Keywords Film thickness Contact line Partially wetting cylinder Lubrication theory Simulation

PRODUCT ENGINEERING

General context, scientific issue

The withdrawal process of a cylinder from a liquid is encountered in a wide range of applications. Previous studies focus on completely wetting cylinders, while film deposition on partially wetting cylinders is the object of only a few investigations.

Methodology / Experimental approach

The volume-of-fluid (VOF) method will be used to simulate the film deposition process on a partially wetting cylindrical surface to capture the profile of film thickness and velocity. The simulated film thickness will be compared with the literature to optimize the distribution and number of meshes in the computational domain, the simulation parameters, and the convergence stability, so that the simulated results can accurately describe the film formation and transition process.

The lubrication theory for film flows is widely used in fluid dynamics. It is based on the assumption that the flow is almost unidirectional. Specifically, the lubrication theory on the cylindrical surface has the following dimensionless form:

$$\frac{\partial k}{\partial x}=1+\frac{3f(d)}{h\left[h+3\lambda(1+d/2)f(d)\right]}\left[\frac{Q}{h^2((1+d/2))}-Ca\right]$$

$$k=\frac{\partial^2 h/\partial x^2}{\left[1+(\partial h/\partial x)^2\right]^{3/2}}-\frac{1}{(r_0+h)\left[1+(\partial h/\partial x)^2\right]^{1/2}}$$

$$f(d)=\frac{8d^3(2+d)}{3\left[4(1+d)^4\ln(1+d)-d(2+d)(2+6d+3d^2)\right]}$$

$$d=\frac{h}{r_0}$$

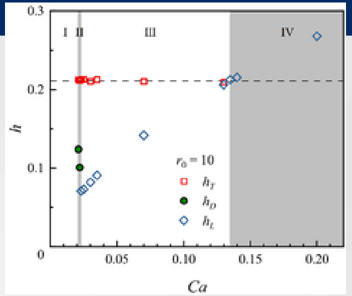
The lubrication theory can be rationally simplified based on the film distribution obtained from the simulation, and then the simplified lubrication equation is solved numerically to get the film distribution and the critical capillary number.

Table Captions for the parameters involved in the above equations

k	Curvature of the film	h	Film thickness	λ	Slip length
Q	Flow rate	Ca	Capillary number	r_0	Cylinder radius
x	Height with regard to the horizontal liquid surface				

Objectives and stakes

The objective of this PhD is (i) to provide a complete description of the flow regimes in terms of the air-liquid interface profile upon withdrawal of a partially wetting cylinder from a Newtonian fluid; (ii) to investigate the film transition mechanism between different regimes and to relate the critical capillary number with the cylinder radius and the liquid property; (iii) to study the film formation mechanism in each flow regime and to relate the film thickness with the cylinder radius and the liquid property.



Evolution of thickness of the thick film hT, the dimple hD, and the thin film hL with Ca for r0 = 10

Main results

The film deposited on a partially wetting cylinder can be divided into four successive flow regimes in terms of the air-liquid interface profile: (I) a stationary meniscus, (II) a thick film connected to the liquid surface through a stationary dimple, (III) a thick film connected to the liquid surface through a capillary ridge and a thin film and (IV) a monotonic film. The critical capillary numbers of the transition between different regimes are controlled by the cylinder radius.

The height of the stationary meniscus xcl in regime I increases with the capillary number and cylinder radius. The thick film thickness hT is influenced by the cylinder radius but not the capillary number. Put it differently, the values of hT in regimes II and III are the same. The thin film thickness hL in regime III is thinner than hT and increases with the capillary number and cylinder radius. The lubrication leads to a good estimation of xcl, hT, and hL for regimes I-III. For regime IV, hL is larger than hT, the lubrication theory is invalid.

References

[1] GAO P et al., J Fluid Mech 2016, 791: 358-83.
[2] QIAN T et al., J Fluid Mech 2006, 564: 333–60.
[3] SNOEIJER J H et al., Phys. Fluids 2006, 18(2): 021701.

LRGP
LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

UNIVERSITÉ
DE LORRAINE

cnrs

EMPP
Énergie Mécanique
Procédés Produits

https://lrgp-nancy.cnrs.fr https://www.univ-lorraine.fr https://www.cnrs.fr/fr https://empp.univ-lorraine.fr

Find our news on LinkedIn !

https://www.linkedin.com/company/lrgp-nancy/