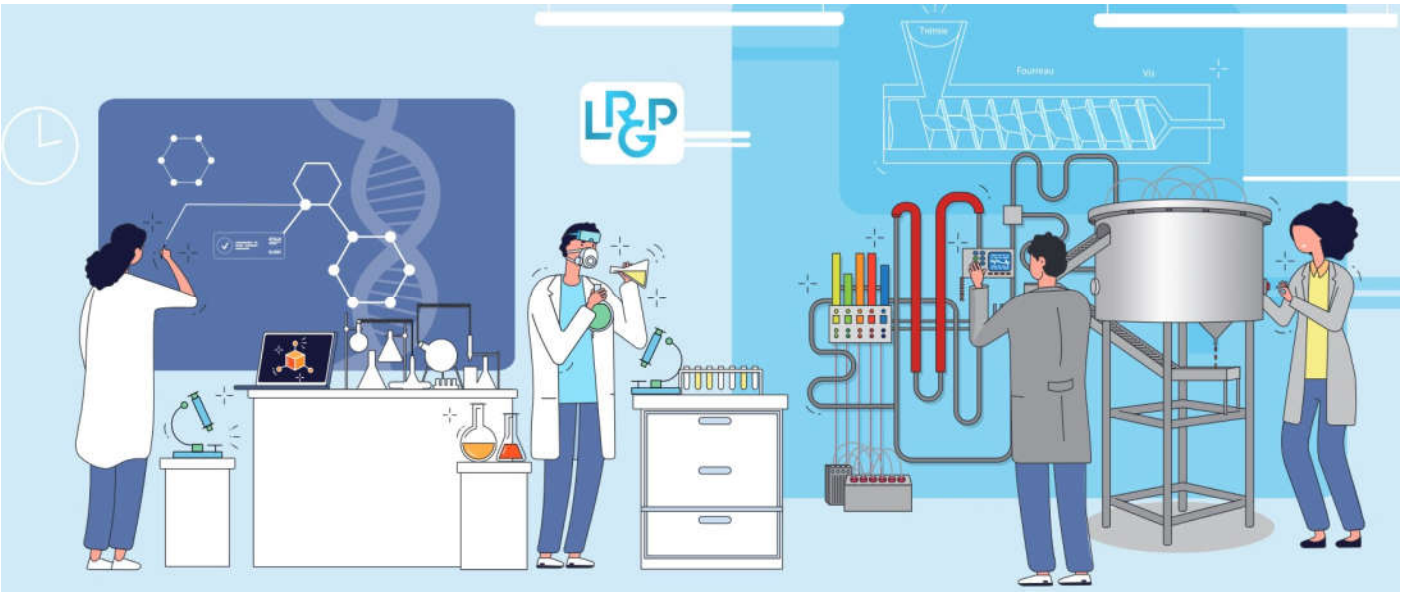


PRESENTATION OF PHD AND POST DOCTORAL RESEARCH WORK

2022

REACTIONS AND CHEMICAL ENGINEERING LABORATORY

UMR7274 CNRS—UL

NANCY





Presentation of PhD and post-doctoral works at LRGP

This document presents the work of doctoral and post-doctoral students carried out during 2022 at the Reactions and Chemical Engineering Laboratory (LRGP, Laboratoire Réactions et Génie des Procédés)

The document was concisely written in order to make it easier for the reader to quickly find out what is done at LRGP. For each study, a summary page presents (1) the general context of the work, (2) the objectives and challenges, (3) the methodology being developed, (4) a schematic illustration, (5) the main results and (6) some references.

All PhD and postdocs research projects currently carried out in the laboratory regardless of their current progress are introduced in this document. Studies, which were recently started, are described by their expected results only while the findings of more mature projects are illustrated with the most significant results

These scientific works are organized into 5 sections according to the different Research Departments at LRGP, as following:

- PERSEVAL : Processes for Environment, Safety and Resource Valorization
- PRIMO : Intensification, Optimization and Architecture of Processes
- BIOPROMO: BioProcesses - BioMolecules
- CITHERE: Kinetics and Thermodynamics for Energy
- Génie des Produits: Product Engineering

Within each Department section, the research projects were further sorted by alphabetic order according to the researcher's surnames instead of year because different new studies begin throughout the year. Moreover some projects may progress faster or slower depending on whether they are in the continuity of previous studies or they initiate a new topic.

I wish you a pleasant reading !

Laurent FALK
Director of Reactions and Chemical Engineering Laboratory, Nancy, France

Presentation of the laboratory

The Reactions and Chemical Engineering Laboratory (LRGP) is a joint unit of CNRS (National Center for Scientific Research) and Université de Lorraine.

On January 1, 2022, the laboratory had a 300-plus workforce, including 15 CNRS researchers, 82 research professors and lecturers, 35 technical and administrative employees as well as about 180 non-permanent staff (researchers on contract and post-doctoral fellows, more than 90 doctoral students, 65 Masters).

The Process Engineering and Reactions Laboratory (LRGP) develops the necessary scientific and technological knowledge for designing, studying, running and optimising the complex processes of physicochemical and biological conversions of mass and energy. Its themes therefore incorporate the conventional scope of chemical engineering via study of the coupled processes of transfer of mass, heat and flows, physical chemistry, such as kinetics and thermodynamics, and biology, with consideration of the complex inter-dependencies and interactions between processes at different spatial and temporal scales. This integrative approach encompasses a growing dimensional spectrum ranging, on the one hand, from nano and micro-scales for improving the consideration of local phenomena, including by integrating or developing the very fundamental approaches of physics, quantum chemistry or biology to, on the other hand, large systems, at the scale of the reactor, process, plant or even territory.

Broadly speaking, the backbone structuring the approaches explored at the LRGP includes:
• detailed knowledge of processes at micro- and even submicroscopic level (detailed chemical or biochemical kinetics, statistical physics, etc.);
• the multi-scale approach to progress from this local knowledge to knowledge and control of the process, and of the plant even;
• the development of robust metrology at an increasingly local scale, implemented to meet the objectives of the first two approaches and to be able to control the processes.

The applications studied are multiple and are geared towards the societal implications of conversion processes, and more generally of a cleaner, safer plant of the future, which is resource-efficient (energy, fossil fuels and mineral resources) and practises waste recovery, conversion of bio-based products and synthesis of recyclable materials and products. The laboratory's research activities thus bear on, for example:

- improving the effectiveness of conversion and treatment processes via the integrated management of mass and energy flows enabling the recycling and recovery (eco-design) of by-products (low-level energy and waste);
- reducing the carbon footprint of conversion processes by using bio-based and petroleum-based resources, cutting back on process water consumption, recycling and reducing pollution, capturing, storing and recovering CO_2 and reducing industrial risks (clean, safe processes);
the synthesis of eco-compatible and recyclable materials and products that are more respectful of humans and the environment as well as designing and developing high-performance complex products (chemical or biochemical) via an organisation at the molecular, macromolecular and colloidal level.

The importance of both the economic aspects of sustainable processes via a life-cycle cost analysis, and the societal aspects via a social life-cycle assessment is also factored in

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 gas-liquid contactors and supercritical processes. The study and development of multifunctional hybrid or coupled processes are thus considered fundamental in a bid to achieve technical and energy efficiency. Intensification, defined as all technologies and methods that enable yields to be increased, and the architecture of processes (Process Systems Engineering) , perceived as the spatial and temporal organisation of unit operations, form the building blocks of the department scientific approach of PRIMO.
The research combines experimental studies on pilots at different scales (intensified micro- and mini-reactors and microstructured systems, catalytic reactors, polymerisation reactors, gas-liquid and liquid-liquid contactors, membrane modules, supercritical extraction processes), specific parametric determinations and computational simulation studies often including computational fluid dynamics (reactive flows in mini-reactors, permanent or cyclic membrane gas separation processes, mass and heat transfer in clothes, evaporators). Beyond the simulation of processes, performed for its specific purpose and for confirming the experimental findings coming from different pilots, the validated models enable identification of processes' optimum working conditions and their control to be studied. Regarding optimisation and control, the research ties in with the general topic of process systems engineering (PSE), bearing both on methodologies (hybrid or global dynamic optimisation, nonlinear and predictive control, control of distributed parameter systems) and their applications (simulation of an adsorption process simulated under pressure via dynamic optimisation, control of reactors, exchangers).

BioProMo – Bioprocesses - Biomolecules

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

CiTherE – Kinetics, Thermodynamics, Energy

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

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

Product Engineering – Process Engineering for Products and Materials

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

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

INDEX

PerSeVal

PROCESSES FOR ENVIRONNEMENT, SAFETY AND RESOURCE VALORIZATION

INDEX

PerSeVal

PROCESSES FOR ENVIRONNEMENT, SAFETY AND RESOURCE VALORIZATION

INDEX

PRIMO - INTENSIFICATION, OPTIMIZATION AND ARCHITECTURE OF PROCESSES

INDEX

PRIMO - INTENSIFICATION, OPTIMIZATION AND ARCHITECTURE OF PROCESSES

INDEX

BioProMo - BIOPROCESSES, BIOMOLECULES

INDEX

BioProMo - BIOPROCESSES, BIOMOLECULES

INDEX

CiTheRe - KINETICS AND THERMODYNAMICS FOR ENERGY

INDEX

CiTheRe - KINETICS AND THERMODYNAMICS FOR ENERGY

INDEX

PRODUCT ENGINEERING

INDEX

PRODUCT ENGINEERING

PERSEVAL

PROCESSES FOR ENVIRONNEMENT, SAFETY AND RESOURCE VALORIZATION

LRP LABORATOIRE REACTIONS

2022

Research subject: Wastewater treatment using novel electro-mixing reactor – comparison with conventional filter press electrochemical reactor

Faidzul Hakim Adnan (Post-Doc)

Emmanuel Mousset

Axe PERSEVAL

Keywords : Electrochemical advanced oxidation, electro-mixing reactor, microfluidic thin film, wastewater treatment, water reuse

General context, scientific issues :

Electrochemical reactor design has not evolved significantly since its introduction in the field of industrial processes in late 18th century **[1]**. The efficiency of an electrochemical process has been governed by either charge transfer or mass transport (the latter in most cases in dilute media). As counter measure, innovations have done either by increasing electrode surface area or mass transport coefficient. For that reason, turbulence promoters as well as different reactor designs such as fluidized and packed bed, submerged multi-jet and flow-through electrodes have been introduced **[2]**-**[4]**. Mass transport intensification could also be achieved with the application of microfluidic electrochemical reactors **[5]**-**[7]**. It would allow the intensification of mass transport coefficient, avoid the addition of supporting electrolyte and significant reduction in energetic consumption. Nevertheless, micrometric electrochemical reactors could not meet the treatment capacity requirement for water treatment application. Moreover, they are more prone to clogging particularly while treating effluents containing high concentration of suspended solids

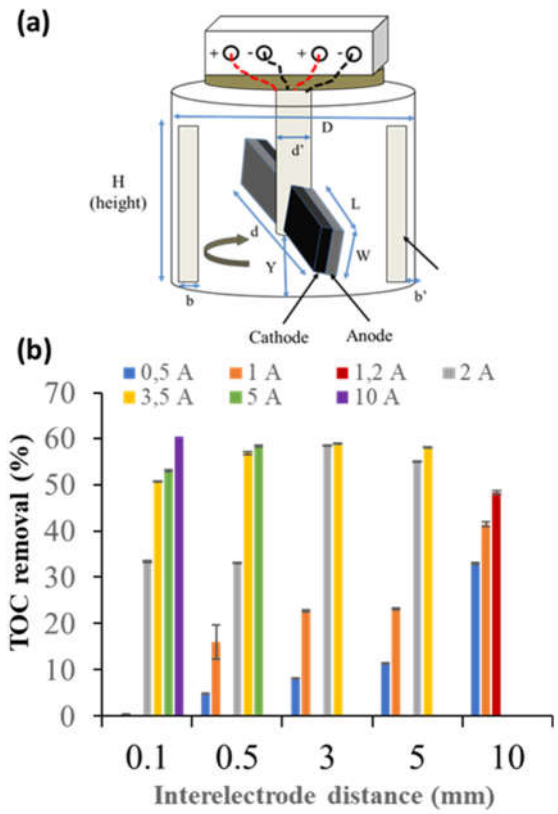
Objectives and stakes :

The purpose of this research work is to introduce a novel electrochemical design that could offer a synergy between microfluidic and macrometric reactor configurations and to develop it at pilot scale with real effluents and on an industrial site, in collaboration with Tree Water company.

Methodology :

The key feature is an impeller with blades called reactive electro-blades. Each blade composes of thin-film electrochemical reactor set in motion within a stirred tank macro-reactor from which the term reactive electro-mixing is adopted **[8]**. The second generation of reactor is under fabrication. In the meantime, experiments with the conventional static filter press cell are currently done. In all cases, paracetamol (0.1 mM) was used as model micropollutant in a synthetic effluent with a conductivity around 1 mS cm^{-1} and neutral pH. Anode and cathode were in stainless steel in both cases, while varying interelectrode distance and current.

Illustration : (a) design of the first generation of reactive electro-mixing reactor and (b) total organic carbon (TOC) removal as a function of the interelectrode distance.



Main results

The interelectrode distance of 0.5 mm demonstrated higher interest by reaching similar TOC removal (60%) at 3.5 A, while the energy consumption was 2.75 lower due to the decrease of resistance at microdistances.

References :

[1] S. Bebelis et al., Chemical Engineering Research & Design, 91 (2013) 1998

[2] E.M. Stuve, Encyclopedia of Applied Electrochemistry, 2014, 568

[3] F. Walsh et al., Analyst 119 (1994) 797

[4] F. Coeuret, Ingénierie des Procédés Electrochimiques, 2003

[5] O. Scialdone et al., Electrochimica Acta, 58 (2011) 463

[6] J.F. Pérez et al., Chemical Engineering Journal, 351 (2018) 766

[7] F.H. Adnan et al., Electrochemistry Communications, 130 (2021) 107097

[8] E. Mousset, Electrochemistry Communications, 118 (2020) 106787

2022

Research subject: EXPERIMENTAL STUDY OF THE CHEMICAL EFFECTS ON THE CLOGGING OF A FILTER IN BUFFERED SOLUTIONS IN THE NUCLEAR INDUSTRY

Coralie Alvarez (3rd year)

Marie-Odile Simonnot

Axe PERSEVAL

Keywords: clogging; chemical effects; filter; LOCA (*Loss Of Coolant Accident*); IRSN

General context, scientific issues :

In the event of a LOCA involving a primary circuit breach, the emergency systems (RIS and EAS) are supposed to ensure reactor cooling and pressure reduction in the reactor containment. These systems are initially supplied by a dedicated water tank. When the lower threshold level in the tank is reached, a "recirculation" model becomes operational. Water collected from the sumps at the bottom of the containment is reintroduced into the reactor core. In the LOCA situation, debris is generated and can be partially transported through the sump filters. This debris can contribute to "physical" clogging. Other effects called "chemical effects" are due to the presence of ions in the solution. These ions result from the debris corrosion and to possible corrosion of the various metal surfaces in the reactor containment. Clogging can lead to failures in the emergency systems and potentially to a severe accident

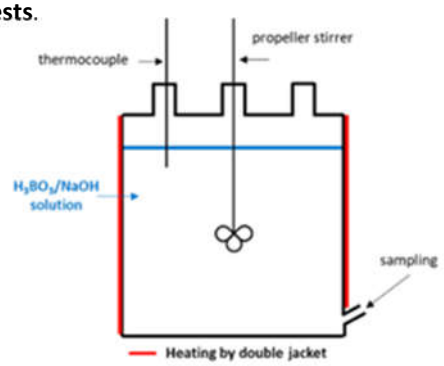
Objectives and stakes :

To ensure the long-term functionality of liquid recirculation, the chemical effects must be understood: composition, conditioning parameters, and their potential effect on clogging. This thesis aims at studying the chemical effects in a dedicated experimental loop by a parametric approach, combined with several chemical and pressure measurements. Solution chemical speciation and precipitate characterization have been performed by ICP-AES, MEB-EDX, IRTF-ATR, DRX, and ToF-SIMS respectively. This work has been carried out at the IRSN in Cadarache , in partnership with the LRGP

Methodology / Experimental approach

The first part is dedicated to static tests to study the potential formation of precipitates under conditions representative of a LOCA (Figure 1). In the second part, dynamic tests are performed in the scaled recirculation loop. An inventory of debris will be injected into this loop using a scaling factor representative of a nuclear power plant. Finally, the results of the static and dynamic tests will be interpreted by a thermodynamic approach using geochemical calculation tools (CHESS). This will enable the consistency between the precipitates obtained and those predicted to be verified

Illustration : : Schematic diagram of the experimental set-up for static tests.



Main results

The first part consisted of the study, under static conditions, of the formation of precipitates likely to occur in a LOCA situation in a boric/sodium buffer. Firstly, dissolution tests of the debris likely to be generated in case of LOCA were performed. The objective was to determine the dissolution kinetics of the elements of interest (Ca, Si and Zn). The tests on the reactivity between Si, Ca, Zn, Na, and B showed the formation of a precipitate composed of silica, calcium borate, borosilicate, and zinc silicate, all amorphous. They were identified thanks to the data from the literature and the various techniques of characterization implemented (SEM-EDS, IRTF-ATR, DRX, ToF-SIMS). The experimental results were compared with those obtained from a geochemical simulation tool (CHESS). The comparison between the experimental data and the simulation results indicates a good overall consistency.

These static tests will be completed by recirculation tests in the COPIN (Clogging Of sumPs In the Nuclear industry) medium-scale experimental loop (Figure 2). This pilot facility has been delivered, upgraded, qualified and experiments are underway.

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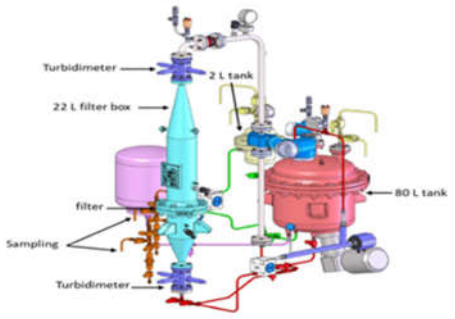
Figure 2 : Schematic diagram of the COPIN filter loop [1]



2022

Research subject: Subject: Recycling of cigarette butts

Katia Begga (Research Engineer)

Cécile Vallières

Axe PERSEVAL | A&C Process

Keywords: Cigarette butts, cellulose acetate, minerals, recycling, process

General context, scientific issues :

Cigarette butts or ends (CE) are a very wide spread waste in the environment. Every second, more than 137000 CB are thrown on the ground [1].

CE is a complex waste containing a lot of toxic substances for both the environment and human being. For this reason, A&C Process in partnership with LRGP and CNRS tries to develop a method to recycle this waste.

Objectives and stakes :

The objective of CERIUM 'Cigarette Ends recycling into useful materials' project is to recover the cellulose acetate and the minerals contained in CE to reuse them and reduce the cigarette ends' nuisances.[

Methodology :

CB is composed of tobacco, ash, paper, and filter. In the filter, about 4000 substances with different quantities are present and some are currently little known [3]. The first step of this project was to study this waste, using several technical analyses such as ICP-AES and TGA and to identify the contained substances.
For the moment, we focus the study on the valorisation of the cellulose acetate present in the filter of CE.
To recycle this component, a series of tests was conducted using different solvents, for example solution of 'sodium hydroxide' selected after a bibliographic review [4]. Several process schemes were tested and their effectiveness were determined by comparing the used filter and the purified filter properties. The more effective process is shown in figure 1.
(Due to confidentiality reasons, no details can be given).
The obtained cellulose acetate is shown in the picture below.

The aim of the developed process is to have the lowest environmental impact. The solvents have to be reprocessed and reused in the recycling of the CE

Illustration :

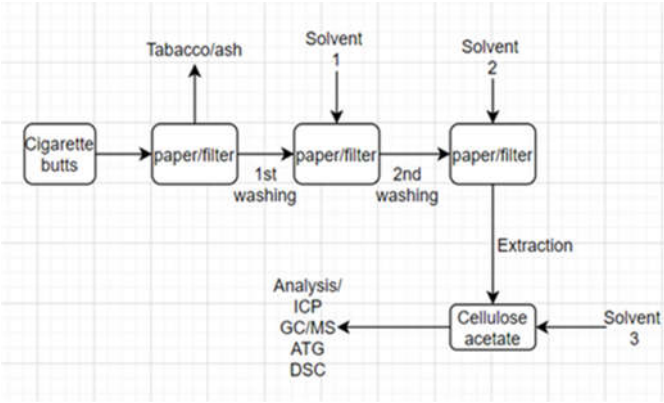


Figure 1 : the followed Process

Obtained acetate

Main results

Thanks to the different technical analysis, we were able to identify (and quantify in case of metals) some substances contained in CE.
For the moment, we have selected a process which allows us to purify the cellulose acetate, this process needs to be optimized before being fully validated and scaled-up
The method of recycling the solvents and the extraction of metals are in progress. Currently, no specific process has been validated. .

References :

[1] https://www.cleanwalk.org/articles/vrai-ou-faux-un-megot-pollue-500-litres-d-eau
[2]https://www.cerium.earth/
[3] A&C Process source
[4] María J. Benavente et al ''Cellulose Acetate Recovery from Cigarette Butts'' 2018

2022

Research subject: PhD subject : Development of an innovative methodology for the determination of the particle size distribution of submicron aerosols

Lizeth Bernal Alvarez (1st year)

Dominique Thomas, Augustin Charvet, Sébastien Bau

Axe PERSEVAL

Keywords: Nanomaterials, Occupational exposures, Particle size distribution, Collection efficiency, Permeance, aerosol

General context, scientific issues :

Numerous scenarios are at the origin of situations of occupational exposure to aerosols of any nature, size, shape, and chemical composition. A large proportion of them are composed in whole or in part of submicron particles, whether aerosols from innovative processes such as additive manufacturing, or more common processes such as welding, thermal spraying, or operations involving manufactured nanomaterials. It is therefore legitimate to assume that the presence of a submicron fraction in aerosols, whatever they are, is ubiquitous.

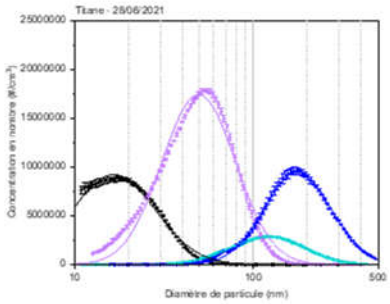
Objectives and stakes :

Particle size distribution is one of the key parameters involved in the characterization of exposure to submicron aerosols. Indeed, the size of inhaled particles is of great interest because it is a determining factor in their deposition in the respiratory apparatus. Furthermore, the particle size distribution is an important parameter for the design of collective protective equipment as well as transport and transfer capabilities.

Methodology :

The characterization of occupational exposure to nanoparticle aerosols requires measurement devices that are often difficult to implement in the field because of their low portability, high cost, complexity of use, and low temporal resolution.
Currently, there is no device for real-time measurement of the particle size distribution of submicron aerosols that is adapted to the field: portable, robust, accessible to non-specialists, and (relatively) affordable. To overcome the lack of such instrument, an alternative solution may be considered, based on the use of different selectors associated to a detector. This approach allows to measure sequentially, different fractions of an aerosol and to determine the particle size distribution over a size range covering 10 nm - 1 µm.

Illustration : Particle size distribution



Main results

Based on the knowledge acquired during previous works conducted at INRS, this PhD thesis aims to:
- identify media allowing the selection of particles,
- characterize the permeance of particles through these media (aerosol measurements, supplemented by physicochemical characterizations of the collected particles),
- set up a theoretical approach, based in particular on a literature review and integrating the physical mechanisms of collection, allowing the description of the permeance curves,
- optimize the approach especially in terms of the number of configurations to be implemented (compromise between number of measurements / accuracy),
- progress on the calculation of the particle size distribution by data inversion methods,
- determine a confidence interval for the output quantities,
- increase the technical ease of implementation of the approach, so that it is suitable for field measurement,
- design the prototype of a "turnkey" tool.

Eventually, the result will be an innovative technical solution for estimating the particle size distribution of a submicron aerosol that can be more easily deployed in occupational atmospheres and that can be distributed within the prevention networks and beyond

References :

Bau, S. and J. Nuvoli (2019). "Combining the Particle Size Selector and a condensation particle counter to determine the number size distribution of airborne nanoparticles." Journal of Aerosol Science **128**: 22-33.

2022

Research subject: Selective recovery of precious metals from waste electrical and electronic equipment (WEEE) by electrochemical methods in ionic liquid

Calogera BERTOLONI (1st year)

Éric Meux (IJL), François Lapicque, Sophie Legeai (IJL)

Axe PERSEVAL

Keywords : Waste electronic and electrical equipments (WEE), precious metals, ionic liquids, deep eutectic solvents, electroleaching, electrodeposition.

General context, scientific issues :

This thesis is part of the EE4Precious project (Electroleaching-Electrodeposition for the recovery of precious metals from waste electrical and electronic equipment), financed by the French National Research Agency (ANR). Indeed, the composition of precious metals in WEEE and in particular in printed circuit boards (PCBs) is higher than that of primary resources. Due to their increasing production, they represent an important economic potential and especially an environmental advantage for the preservation of resources.

However, conventional methods to recover these precious metals use toxic products, dangerous for humans and the environment, so the development of a more environmentally friendly process is necessary

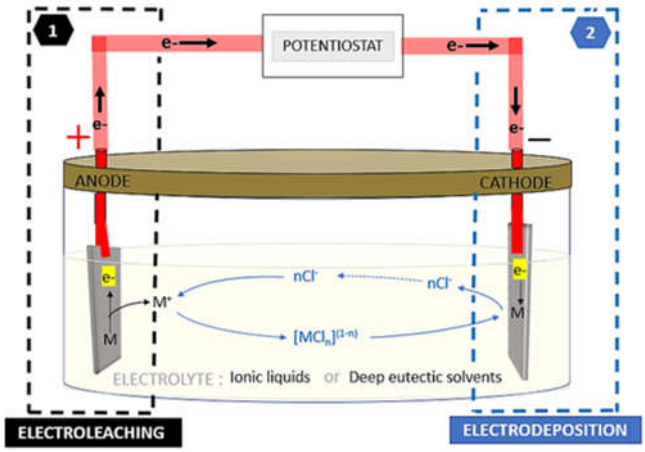
Objectives and stakes :

The thesis work consists of developing an electrochemical process for the recovery of silver, gold and palladium contained in an ultimate metallic fraction, resulting from the processing of electronic boards by the company Terra Nova Development (TND), by developing a method using a softer chemistry than that used in existing processes. This project includes an in-depth study of the electrochemical reactions of anodic dissolution and cathodic deposition of the various metals of interest, with kinetic aspects of charge transfer and mass transfer. The objective is to obtain metallic phases of high purity at the cathode (selectivity) and to implement both reactions with a maximum faradic yield to ensure the sustained recycling of electrolyte.

Methodology :

For this work, the solvents used are ionic liquids (ILs) or deep eutectic solvents (DES), which are non-volatile and not very corrosive. Following the previous studies[1], ethaline 1:2 is the solvent that was mainly chosen. It is a mixture of choline chloride (hydrogen bond acceptor) and ethylene glycol (hydrogen bond donor) with a molar ratio of 1:2 respectively. First of all, the experiments are carried out using pure metal phases, then alloys will be considered, and finally the polymetallic phase resulting from the processing of electronic cards, and a mini pilot will be designed, allowing to come as close as possible to an industrial process. Thus, from silver wire/plate and gold plate, leachates are achieved by chronoamperometry by imposing an oxidation potential or by chronopoten-tiometry by applying a current. So, to study the performance of the electro-leaching, gravimetric yields are determined by mass loss and confirmed by ICP analysis. With respect to electrodeposition, cross-linked electrochemical methods such as cyclic voltammetry, linear voltammetry... are used to study the transport properties (charge transfer, mass transport) of metal species in ethaline. Moreover, the optimization of electrodeposition is developed by varying different parameters such as the concentration of metals in the medium, the deposition mode (at a fixed current or potential). The properties of metals deposited will be investigated using a Hull cell, and finally coupled leaching and deposition steps will be achieved in a pilot.

Illustration : Electroleaching and electrodeposition cell



Main results

Currently, the results are focused on silver. The leaching runs carried out present gravimetric and ICP analysis yields close to 100%. The various electrochemical methods show that the mass transport is the rate-controlling step in this process. Indeed, with the values of rate constant and transfer coefficient are respectively of $7{,}0\times10^{-6}$ cm/s and 1, whereas the diffusion coefficients are in the order of $6{,}23\times10^{-7}$ cm^2/s with a maximum of 20% of variation depending on the techniques used

References :

(1) Villemejeanne, B.; Legeai, S.; Meux, E. 2022. J. Environ. Chem. Eng., 10 (1) : 107063.

2022

Research subject: : Impact of impurities on CO2 capture using PSA

Sayali Ramdas Chavan

Léa Sigot, Cecile Vallières

Axe PERSEVAL | Air Liquide

Keywords : Adsorption process, Gas separation, CO_2 capture, PSA, Impact of NO_x

General context, scientific issues :

Research has been revolving around carbon capture for decades in the context of global warming. One of the popular industrial processes for post combustion CO_2 capture is Pressure Swing Adsorption (PSA) due to its advantages such as low energy consumption, no hazardous by-products and highly efficient automatic operation [1]. Even though this technology is evolved, its operation in presence of impurities such as NO_x and SO_x remains unexplored. Moreover, the numerical modelling of the complex process is challenging task [2].

Objectives and stakes :

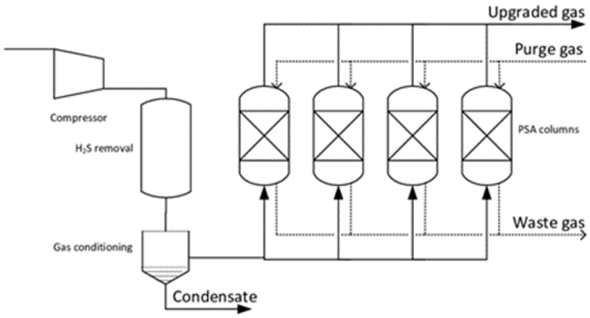
The following study is a joint project between LRGP and Air Liquide in the frame of PIGAZ joint lab. The preliminary objective of this study is to characterise the experimental performance of different types of adsorbents for CO_2 capture in the presence of impurities (NO_x first). The project begins with the conceptualization of the lab-scale pilot followed by its design, construction, experimentation and optimization. Eventually, the work would be expanded to a predictive numerical model to optimize the PSA process

Methodology :

First months were dedicated to the conceptualization of the process. The pipping and instrumentation diagram was also drafted during this period. Accordingly, the instruments have been ordered and parallelly a 3D visualization model, an electrical scheme and electronic circuits are underway.

This test bench will be used to perform PSA type cycles. An example of PSA process for CH_4/CO_2 separation is given in the illustration figure. The minimum requirement is a basic four-stage Skarstrom-type cycle. To improve the cycle efficiency, additional co-current and counter-current balancing stages will be included at the end of the production and purge stages respectively.

Illustration : Graph overview of two-bed PSA system for biogas upgrading [3].



Main results

The tests will be carried out using given process parameters (gas flowrates, feed composition) and their effect on purity and yield will be studied.

An essential aspect of the study will be the ability to precisely quantify the concentrations of impurities (NO_x primarily), CO_2 and oxygen in the (synthetic) feed gas mixture and in the outgoing gas streams during the high-pressure production, depressurization and purge stages. Online monitoring and analysis during these long-term tests will be essential to perform mass balances.

Secondly, it would be necessary to develop a model allowing the reconciliation of experimental data and prediction by simulation of the performance of industrial cycles. For this task, experimental measurements of pure body adsorption isotherms and adsorp-

References :

[1] Xing, Rui, et al. "Vacuum pressure swing adsorption system for N2/CO2 separation in consideration of unstable feed concentration." *Adsorption* 25.6 (2019): 1147-1158.

[2] Sees, Michael D., Toni Kirkes, and Chau-Chyun Chen. "A simple and practical process modeling methodology for pressure swing adsorption." *Computers & Chemical Engineering* 147 (2021): 107235.

[3] Bauer, Fredric, et al. "Biogas upgrading-Review of commercial technologies; Biogasuppgradering-Granskning av kommersiella

2022

Research subject: Coalescence and droplet spreading : multiscale experimental study and numerical simulation

Emile Collignon (2nd year)

Huai-Zhi Li, Xavier Fank

Axe PERSEVAL

Keywords : Numerical Simulation, Lattice Boltzmann Method, Multiphase Flow, Complex Flow, Non-Newtonian fluid, Viscoelastic fluid, Droplet, Spreading

General context, scientific issues :

The recent research showed that negative wake appears during a sedimentation in a viscoelastic fluid [1]. Furthermore, some advances are made in the lattice Boltzmann method for simulation axisymmetric case [2] and viscoelastic fluid [3].

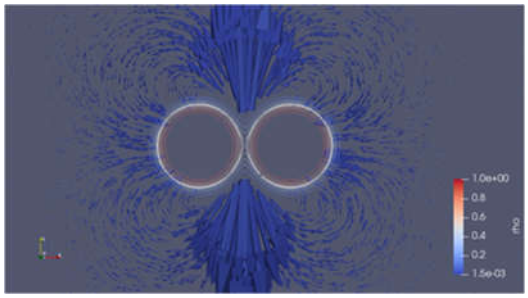
Objectives and stakes :

Actually, the objective is to realize a multiphase axisymmetric with high density ratio code using lattice Boltzmann method to compute viscoelastic dop to recover the negative wake. We also interest in coalescence of two non -Newtonian bubble. And also, to realize an axisymmetric model for a sphere in sedimentation in a non-Newtonian fluid.

Methodology :

The main objective remains to develop an axisymmetric high density ratio lattice Boltzmann method for non-Newtonian fluid. In order to simplify the problem, we need to have a concrete interface. First, we develop an axisymmetric lattice Boltzmann method, then we complete with a Maxwell model for a non-Newtonian fluid. For the multiphase case. The methodology is quit the same. Instead of develop a monophase axisymmetric lattice Boltzmann we develop a multiphase axisymmetric high-density ratio in order to allowed high viscosity ratio and recover real cases.In order to validate the models, we try to recover experimental results from the laboratory.

Illustration : Flow around two coalescing bubbles



Main results

The research take place in a context of improvement of numerical method for viscoelastic fluid and non-Newtonian fluid. We developed an axisymmetric high density ratio multiphase lattice Boltzmann coupled with a Maxwell model. Same for the monophasic case.

We tried to recover the negative wake behind for a bubble and a sphere rising in a viscoelastic fluid

References :

[1] Frank, X., et H.-Z. Li. 2006. « Negative wake behind a sphere rising in viscoelastic fluids: A lattice Boltzmann investigation ». *Physical Review E : Statistical, Nonlinear, and Soft Matter Physics* 74 (056307): 9 pages. https://doi.org/10.1103/PhysRevE.74.056307.

[2] Li, Q., He, Y.L., Tang, G.H., Tao, W.Q., 2010. Improved axisymmetric lattice Boltzmann scheme. Phys. Rev. E 81, 056707. https://doi.org/10.1103/PhysRevE.81.056707

[3 Wang, Di, Danielle Tan, et Nhan Phan-Thien. 2019. « A lattice Boltzmann method for simulating viscoelastic drops ». *Physics of Fluids* 31 (7): 073101. https://doi.org/10.1063/1.5100327

2022

Research subject: Modelling and simulation of micropollutant removal in the wastewater treatment plants and dedicated post-treatments

Thi Mai Lan Duong

Olivier Potier

Axe PERSEVAL

Keywords : micropollutant removal, wastewater treatment, activated sludge, biodegradation, modelling, hydrodynamic and kinetic models, post-treatments.

General context, scientific issues :

Micropollutants (MPs) are low-concentration but hazardous pollutants from pharmaceutical products, pesticides, etc., and for the past decades, they have been considered as a source of risk for public health and the environment. Being a main source of discharging these pollutants into the environment, wastewater treatment plants (WWTP) are therefore receiving more and more attention for performance improvement research, especially for MPs removal. In addition to laboratory and pilot experiments, mathematical models are also essential tools for the design and the optimization of the new processes.

CoMinGreat is a project financed by INTERREG for the study on the treatment of micropollutants in the wastewater of the Greater Region (Luxembourg, Belgium, Germany and France). By financing projects from European Regional Development Fund (ERDF), the European Union program INTERREG supports and promotes cross-border cooperation. Its main aim is to solve common challenges and find shared solutions in different fields such as health, environment, research, education, transport, sustainable energy and more.

Objectives and stakes :

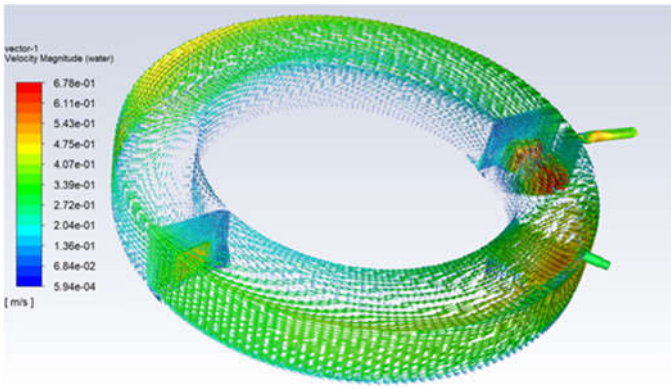
Being a sub-part of the CoMinGreat project, the mission of this work is to modelling and simulating the removal of micropollutants of the Bliesen's waste water treatment plant (WWTP) in Germany. The goal is not only the simulation of the biological treatment system but also the different post-treatment methods that have recently been installed and tested at the plant.

Methodology :

WWTP: The studies are based on the WWTP of Bliesen, a city in Germany. It has been in service since May 1994 to treat wastewater with a capacity of 13,000 population equivalent and a flowrate up to 7,800 m³/d. The plant proceeds the mechanical, biological and chemical cleaning stages by the pretreatment and secondary treatment systems (biological reactor and decanter) without primary clarification. Moreover, 4 different processes of post-treatment are recently installed at the plant and are being tested by the other partners of the Interreg program, including a Constructed Wetland, PhotoFenton followed by Constructed Wetland, GAC columns and Ozonation column followed by GAC columns. In this project, the simulation focuses on the elimination of micropollutants through secondary treatment and post-treatments.

2. Model: For biological reactors, the models used must take into account 2 important processes: the hydrodynamics of the reactors and the kinetics of the MPs biological elimination reactions. A bibliographical search was carried out first, to study all types of MPs removal kinetics (especially in different anoxic and aerobic conditions) and the complex hydrodynamics of the station's reactors. On the other hand, necessary data for a detailed understanding of the operation and configuration of the station have been collected, allowing the development of the basic model on the programming software. Compartmental model approach with a study on CFD is carried out to better present local mixing and turbulence in the large reactor. Afterward, for the post-processing simulations after collecting the data on the operation and configuration of the processes, also the experiments results (residence time analysis for some cases), its models will be developed on the programming software.

Illustration : Water velocity magnitude of the biological reactor (Computational Fluid Dynamics simulation)



Main results

Kinetics of the micropollutant elimination reactions: according to research, it appeared for some micropollutants, biodegradation is not sensitive to the presence or absence of oxygen, whereas for others, they are better degraded in aerobic condition than in anoxic condition.

2. Simulation program: The model is developed on the programming software including the kinetic and hydrodynamic processes from basic to complex model. For secondary treatment systems, the complex kinetic model integrating the different anoxic/aerobic mixing zones and the different behaviours of micropollutants in 2 conditions has been included. Other part, the hydrodynamic models were programmed thus providing the basic structure of the simulation program (rectangular reactor with recycle of mixed liquor).

3. Fluid dynamics simulation: The simulation of the real size reactor integrating the vertical propeller movement, with/without aeration system provide a better presentation of waterflow and turbulence behaviour of the biological reactor in aerobic/anoxic condition (illustration). The simulation of residence time distribution will then give the "virtual" ideal reactors in cascade, allowing the fine description of the hydrodynamics of the reactor.

References :

1] Hatoum R. (2019). *Removal of micropollutants with activated sludge: proposition of a new kinetic model and special focus on hydrodynamic reactor configuration and local mixing*. [Unpublished doctor's thesis]. University of Lorraine.

[2] Pomiès M., Choubert J.- M., Wisniewski C., Coquery M. (2013). *Modelling of micropollutant removal in biological wastewater treatments: A review*. Science of the Total Environment 443, p.733–748.

[3] Suarez S., Lema J.M., Omil F. (2010). *Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions*. Water Research 44, p.3214–3224.

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2022

Research subject: Biomimetic Reactor : Coupling the Regeneration of NADH to the Oxidation of Hydrogen

Wassim El Housseni (3rd Year)

Dr. Francois Lapicque (LRGP) & Dr. Mathieu Etienne(LCPME)

Axe PERSEVAL

Keywords : NADH, Hydrogen, Proton exchange membrane fuel cell (PEMFC), Mass transport, CP-MWCNT Gas diffusion electrode (GDE), CP-MWCNT-FNR, CP-MWCNT-LDH

General context, scientific issues :

Biocatalysts such as oxidoreductase enzymes offer exquisite selectivity under mild reaction conditions, but have proved difficult to exploit in electrosynthesis for fine chemical production. Many of the enzymatic reactions catalyzed by oxidoreductases require a hydride transfer from the expensive biological NAD(P)H cofactor. In consequence, the application of these enzymes for enzymatic bioconversion requires the recycling of the cofactor in order to make the process economically viable. The electrochemical regeneration of the cofactor is possible, but problematic at unfunctionalized electrodes due to the formation of non-active form of the cofactor . The immobilization of an electrochemical or an electro-enzymatic redox mediator onto an electrode surface allows the regeneration of the active form of the cofactor (NAD(P) H) at much more modest potentials than using the unmodified electrode

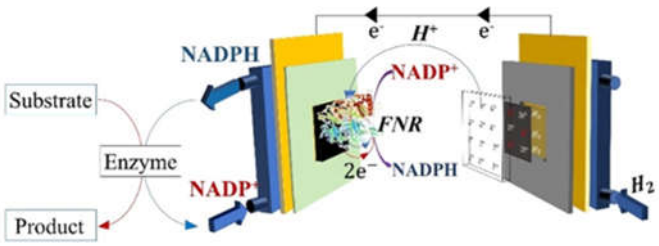
Objectives and stakes :

Our objective is to combine the electrochemical regeneration of NADH mediated by FNR covalently immobilized on a carbon paper with MWCNT (CP-MWCNT-Rh) at the cathodic compartment, the application of continuous flow reaction, and the hydrogen oxidation using a GDE at the anodic compartment in a single system. The system will be then coupled to an enzymatic reaction for the bioconversion of pyruvate mediated by LDH

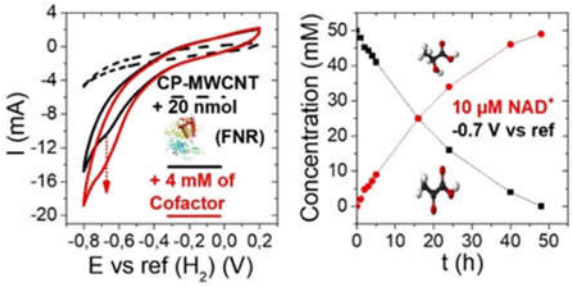
Methodology :

This approach has been feasible using a bioreactor that couples the reduction of NAD+ to the catalytic oxidation of hydrogen. A nafion membrane has been placed between the anodic and the cathodic compartments allowing the passage of H+ from the anodic to the cathodic compartment. To optimize the proposed process, various factors have been varied e.g. pH, the activation procedure for the carbon-based electrode, as well as the cell operating conditions such as the hydrogen and the solution flow rates.[2]In a second step, FNR has been immobilized on a CP-MWCNT for the regeneration of NADH. Finally, lactate dehydrogenase has been immobilized on CP-MWCNT for the bioconversion of pyruvate

Illustration : Functional scheme of the bioelectrochemical reactor



Main results



The first objective in this study was to validate the stability of FNR immobilized in a CP-MWCNT.

The electrochemical activity of the CP-MWCNT-FNR was evaluated through cyclic voltammetry at a scan rate of 5 mV/s and with hydrogen and solution flow rates of 20 mL/min. Results showed (Figure on the left) that the CP-MWCNT-Rh kept on its activity for more than 6 days with a cathodic peak of 4.5 mA. The addition of $NAD(P)^+$ exhibited an increase in the current related to the reduction of NADP+ by FNR

After validating the stability of the CP-MWCNT-FNR, the system was coupled to the bioconversion of pyruvate in the presence of a CP-MWCNT-LDH. The study of the bioconversion of 50 mM of Pyr in the presence of 10 µM of $NADP^+$ (Figure on the right) showed a decrease of concentration of pyruvate with time and an increase in the biosynthesis of lactate. 50 mM of lactate were synthetized after 48 h which proves the activity of both the FNR and LDH systems toward the regeneration of NAD(P)H followed by the bioconversion of pyruvate.

References :

1] Zhang, L.; Etienne, M.; Vilà, N.; Le, T. X. H.; Kohring, G.-W.; Walcarius, A. Electrocatalytic Biosynthesis Using a Bucky Paper Functionalized by [Cp*Rh (Bpy)Cl] + and a Renewable Enzymatic Layer. *ChemCatChem* **2018**, *10* (18), 4067–4073.

[2] El Housseini, W., Lapicque, F., Walcarius, A., & Etienne, M. (2021). A hybrid electrochemical flow reactor to couple H2 oxidation to NADH regeneration for biochemical reactions. *Electrochemical Science Advances*, e202100012

2022

Research subject: Lifting the fog off fuel mist explosions: a new procedure to determine the ignitability and explosivity of mist releases

Stephanie El-Zahlanieh (3rd year)

Olivier Dufaud

Axe PERSEVAL | INERIS

Keywords : Lifting the fog off fuel mist explosions: a new procedure to determine the ignitability and explosivity of mist releases

General context, scientific issues :

The chemical and petrochemical industries have witnessed a significant number of explosions triggered by involuntary oil mist releases. Such inadvertent releases can lead to the formation of a flammable mixture that can cause an explosion in the presence of an ignition source. ATEX Directives recognize the possible threat posed by mists. However, there is still a lack of tools to assess explosion risks related to mists and only a limited amount of information is available on how to estimate the degree of the threat posed by high-flashpoint (FP) fluid mists and the type of ATEX equipment to use. It also became evident that mist explosions can occur at temperatures below the FP of the aerosolized liquid [1,2] and that, although ATEX standards recognize the dangers of flammable mists, liquid categorization is still limited to this FP. Indeed, while the classification of flammable gases and dust is well-established, that of liquid aerosols remains less so

Objectives and stakes :

The increased interest and concern in preventing and mitigating mist explosion incidents call for a standardized test method to evaluate such risks and a greater understanding of the influence of external conditions. This work, therefore, aims to propose a complete procedure allowing the evaluation of the ignition sensitivity and the explosion severity of fuel mist clouds.

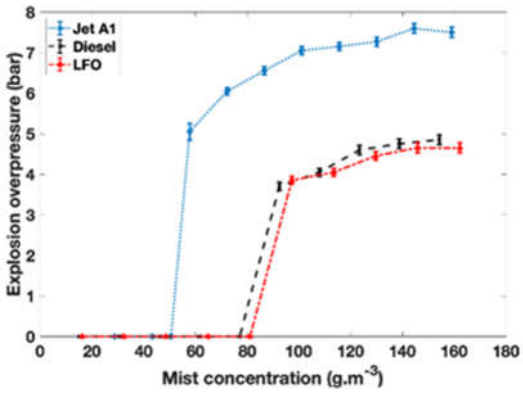
Methodology :

Based on the 14034 European standard series for the determination of explosion characteristics of dust clouds, this study proposes a test method for the experimental determination of the minimum ignition energy (MIE), the lower explosive limit (LEL), the maximum explosion pressure Pmax, and the maximum rate of pressure rise dP/dtmax in a single already-standardized test vessel. The selected test vessel was a closed 20 L explosion sphere in which mists were injected using a Venturi-based spray nozzle. Seven fluids were chosen, characterized, and tested. Experiments were performed to prove the feasibility of this proposed test procedure and to highlight the necessity of high-flashpoint fuel mist classification

References :

[1] Eckhoff RK. Chapter 3 - Explosions in Clouds of Liquid Droplets in Air (Spray/Mist). In: Eckhoff RK, editor. Explosion Hazards in the Process Industries, Gulf Publishing Company; 2005, p. 149–73.
[2] Eichhorn J. Careful! Mist can explode. Petroleum Refiner 1955;34(11):194–6.

Illustration : Variation of P_m of LFO, diesel, and JetA1 mists



Main results

The figure demonstrates the evolution of the explosion overpressure as a function of mist concentrations at T = 40 °C. Jet A1, diesel, and LFO mists of mean droplet diameters of about 9 µm exhibit a capability to explode, once ignited with 100 J chemical ignitors. Tests on other fluids were also performed under different experimental conditions. The influences of the initial temperature, injection pressure, concentration, and droplet size distribution (DSD) were all assessed. The table below also demonstrates findings of the LEL and the MIE of the fuel mists at ambient T and a DSD between 8 and 10 µm. This study is a step forward toward establishing a standardized procedure to test mist cloud explosions. It proposes a procedure using a single apparatus available in most laboratories, accepted by researchers, standardized, and proven to be versatile. The reproducibility and repeatability of this test method were verified with hundreds of tests. This test method is appropriate for mist explosion testing and adaptable to industrial or conservative parameters.

Fluid	LEL ($g.m^{-3}$)	MIE (J)
Ethanol	77	< 0.1
Isooctane	64	< 0.1
Jet A1	94	0.2
Diesel	123	0.3
LFO	113	0.3
Biodiesel	103 (5 kJ)	5000
Mobil DTE	No ignition	> 10000

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2022

Research subject: MOFS potentials for air purification from Volatile Organic Compounds mixture in presence of humidity

Mathilde FRANÇOIS (3rd year)

Cécile VALLIÈRES |Léa SIGOT

Axe PERSEVAL

Keywords : Electrochemical advanced oxidation, electro-mixing reactor, microfluidic thin film, wastewater treatment, water reuse

General context, scientific issues :

Metal-Organic Frameworks (MOFs) are microporous materials interesting for purification and separation processes by adsorption. They differ from common adsorbents by their mixed organic/inorganic (metallic) structure which gives them suitable properties for various applications (adsorption, catalysis, etc.) [1, 2]. In addition, volatile organic compounds (VOCs) are natural or anthropogenic compounds emitted in- and outdoors from several sources (manufacturing industries, cleaning products, etc.) which can involve health or environmental problems when they are present in too high concentrations (the concentration threshold is specific to the VOC) [3, 4]. Therefore, VOCs researches tend toward the elimination of these compounds. This study focuses more specifically on the treatment of indoor air by an adsorption process involving MOFs

Objectives and stakes :

The purpose of this research work is to introduce a novel electrochemical design that could offer a synergy between microfluidic and macrometric reactor configurations and to develop it at pilot scale with real effluents and on an industrial site, in collaboration with Tree Water company.

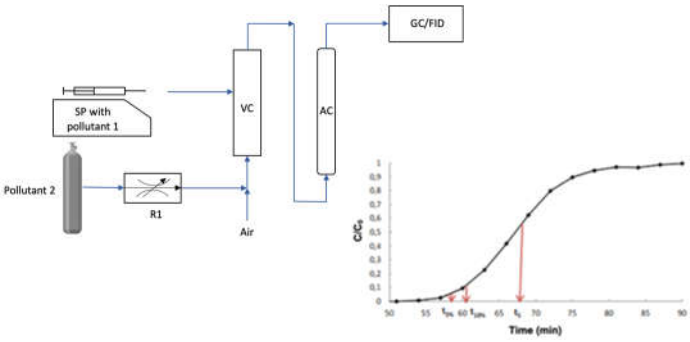
Methodology :

As a first step, the adsorbent needs to be characterized to understand the structure, and hence the porosity, to potentially anticipate the interactions between the MOF and the studied VOCs. The textural characterisation is obtained by static measurements of N_2 adsorption at 77 K and provide adsorption isotherms. In addition, adsorption isotherms with water and single pollutants are performed to observe the behaviour of the MOF with these molecules.

The second step of the work is the study of dynamic adsorption of the VOCs on the MOF. The dynamic measurements are conducted on a lab-scale pilot to obtain breakthrough curves (C/C_0 as a function of time, with C/C_0 being the ratio between the concentration C at a time t and the adsorption column inlet concentration C_0) (see below).

A parametric study is made by changing the pre-treatment of the MOF and also by experimenting VOCs mixtures and regeneration of the MOF by adsorption/desorption cycles.

Illustration: Experimental lab-scale pilot and breakthrough curve



Dynamic measurements of VOCs adsorption on HKUST-1 are performed with this pilot. Succinctly, air is used as carrier gas and allows the transport of the VOC gases diluted at the required concentration. Pollutants are generated into a vaporisation chamber (VC) by a syringe pump (SP), if they are injected from the liquid phase, or with a gas cylinder. The VC can also act as a mixture chamber of the VOCs with air. Then, the gas mixture goes through the adsorption column (AC) where the adsorbent is placed, and the purified stream is finally analysed by gas chromatography (GC) coupled with a flame ionisation detector (FID). The GC/FID is used to quantify the concentration of VOCs at the column outlet and deduce the quantity adsorbed by the MOF, thus the adsorption capacity of the MOF.

Expectations

The main expected result is to prove the interest of using HKUST-1 as an adsorbent for the adsorption of VOCs present in indoor air at too high concentrations. The final pilot-scale process should lead to high adsorption capacities with an optimised pre-treatment of HKUST-1. Moreover, an optimised granulometry of the adsorbent is expected to improve the VOC adsorption kinetics. The possibility to regenerate the MOF in order to perform several adsorption/desorption cycles is another objective to make the process competitive with common adsorbents.

References :

[1] M. Bahri et al., *Chem. Eng. Jour.,* 2017, 313, 711-723

[2] P. Falcaro, *Chem. Soc. Rev.*, 2014, 43, 5513-5560

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[7] T. R. C. Van Assche, *J. Phys. Chem. C,* 2013, 117, 18100-18111

2022	**Research subject: Development of an environmentally friendly lithium capture technology**	
	Pierre Latraye (Ingénieur de recherche) Nathalie Bardin-Monnier, Augustin Charvet Axe PERSEVAL	

Keywords : Fluid Mechanics, Numerical simulation, lithium capture, CFD

General context, scientific issues :

This work is part of a European project « LiFE », which aims to develop the EU's sovereignty over the lithium value chain, including control of supply. Europe only produced 3% of its demand in 2020.

Installations such as geothermal wells or oil wells use a large volume of water in their extraction process. This water contains a large quantity of lithium which is not exploited.

With the help of various partners and under the direction of GEOLITH, the goal is to develop a process capable of extracting this lithium in an ecologically responsible way.

Objectives and stakes :

The main objective is to contribute to the development of a cartridge that can be simply grafted to geothermal installations. This technology has the ambition to be:

- an economically competitive solution, guaranteeing Europe prices aligned with the market.
- an eco-responsible technology, that respects European environmental standards: no waste production, no carbon emissions, and no water waste.
- a ready-to-use technology
- a protected, scientifically robust technology

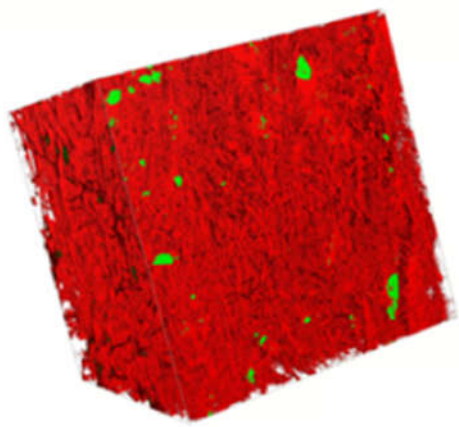
Methodology :

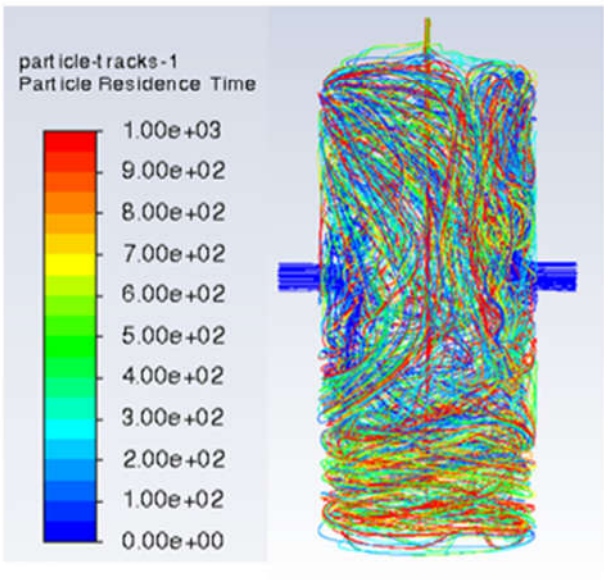
First, the flow simulations through the different materials likely to compose the cartridge is realized to characterize the material's permeability according to its composition and structure. The main goal is to find the most adapted to the realization of the cartridge.

After having determined the composition of the cartridge, the tests of various flow models according to the operating conditions envisaged (flow rates to be treated, admissible velocity) are performed and compared to existing experiments to select the best one.

Finally, several tests of different cartridge designs (radial or longitudinal) are launched to optimize the flow.

Illustration : 3D-Reconstruction of a sample of fibrous medium





Particle residence time in a cartbridge (s)

Main results

The different numerical studies realized in LRGP with the help of tomographic images made by a partner and the different experiments carried out in the laboratory help us calculate the permeabilities of the different materials and compare the flows in different types of cartridges.

With these results, LRGP can advise its partners on the choice of fibrous medium and cartridge geometry.

2022

PhD subject : Efficiency of filtration under humidity of metallic medium

Marie Lecoq (4th year)

Dominique THOMAS, Soleiman BOURROUS, Jean-Christophe APPERT COLLIN

Axe PERSEVAL | IRSN

Keywords : metallic filter, liquid aerosol, pressure drop, efficiency, multilayers

General context, scientific issues :

In the case of an accidental scenario producing vapour (leading to a liquid aerosol), in a confined space, the filters present in the ventilation network could present a decrease of their filtration efficiency. Moreover, a quick and important increase of their pressure drop can lead to their rupture, and thus to an unexpected release of contaminant into the atmosphere. The solution considered to avoid this failure consists in the installation of a metal filter, more resistant, upstream of these filters (made of glass fibres).

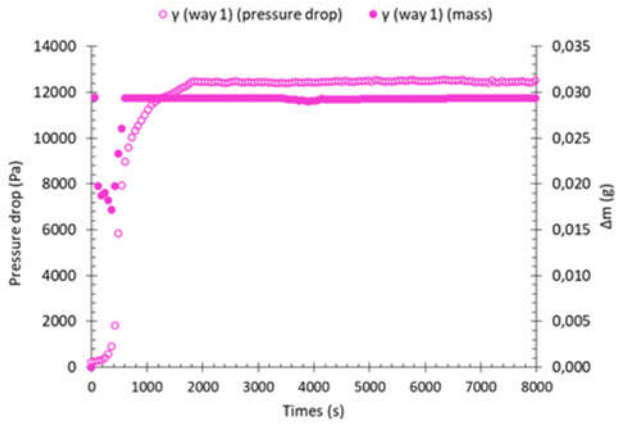
Objectives and stakes :

The objective will therefore be to relate the physico-chemical properties of the liquid and the structure of the metallic media, to the pressure drop elevation and to the amount of liquid accumulated at saturation. To do this, we will carry out analytical experiments with different liquid aerosols and different filters with controlled properties

Methodology :

The metal filters are composed of one or more layers of fibres of different characteristics (in terms of fibre diameter, compactness or thickness). These filters have been previously characterised by analysing SEM images and the characteristics obtained are: the average diameter of the fibres is between 1 and 13 µm, the thickness varies between 30 and 300 µm and the packing density is between 0.30 and 0.50. These sintered layers increase the resistance of the filters to the mechanical stresses associated with the shaping of the filter (such as pleating of the media). These multilayer media can also be of interest in terms of filtration performance (pressure drop and efficiency). The multilayer media studied differ in the nature of the layers and the arrangement of the layers. Two types of layer arrangement were studied: a so-called "symmetrical" arrangement (i.e. identical layers are superimposed on either side of the central layer which serves as an axis of symmetry) and a so-called "asymmetrical" arrangement as illustrated. After studying the pressure drop and efficiency of the media layers separately, the multilayer filters were clogged with a liquid aerosol. The DEHS aerosol is produced by means of an atomiser and is applied to the filter by suction. The filtration rate is kept constant during the loading of the filter. A pressure drop sensor is placed around the filter to monitor the pressure drop. A meter is placed upstream and then downstream of the filter to measure the aerosol concentration and particle size distribution of the aerosol. The filter is also weighed before and after each test to determine the mass of liquid accumulated in the filter.

Illustration : Pressure drop and mass evolution for multilayer filter to filtration rate 6 cm/s.



Main results

The results presented above show the evolution of the pressure drop and the mass collected per time step, for a multilayer filter, at a constant filtration speed of 6 cm/s (figure 1). The evolution of the pressure drop of metal filters for a DEHS aerosol is characteristic of that of a wettable filter. In the literature [1] [2], the pressure drop evolves in a quasi-linear manner, before increasing exponentially and stabilising at filter saturation (a behaviour that has been observed when each layer is individually sealed). In contrast, for multilayer metal filters, a further inflection of the pressure drop is evident between the exponential rise and its stabilisation. This inflection starts when the mass of liquid collected per time step stabilises (figure 1). Thus it can be assumed that before this inflection point the media layers saturate one after the other, until the most effective layer is reached. Then after this inflection point the liquid will migrate into the downstream (less efficient) layers (without saturating them) in order to be drained. These layers have the role of improving the drainage, and are called in the literature a drainage layer [3].

References :

[[1] ''Etude de la filtration des aérosols liquides et de mélanges d'aérosols liquides et solides'' Tom FRISING (2004), Thèse INPL

[2] ''Pressure drop and liquid transport through coalescence filter media used for oil mist filtration'' D. Kampa, S. Wurster, J. Buzengeiger, J. Meyer, G. Kasper (2014), International Journal of Multiphase Flow

[3]"The effect of a drainage layer on filtration performance of coalescing filters" C. Chang, Z. Ji, F. Zeng (2016), Separation and Purification technology

2022

Research subject: Multiscale approach for multiphase flows in the presence of interfacial phenomena

Hao Li (3nd year)

Huai-Zhi LI

Axe PERSEVAL

Keywords : multiscale flow, interface phenomenon, multiphase flow, Particle Image Velocimetry

General context, scientific issues :

Multiphase flows are commonly encountered in both nature and many industrial sectors [1,2]. Former important works in process engineering are often global results such as gas retention rate, distribution of sizes, therefore in the sense of the black box and in the form of empirical correlations. The phenomena of formation, interactions and coalescence between bubbles or drops in liquids of different nature are still poorly understood [3,4].

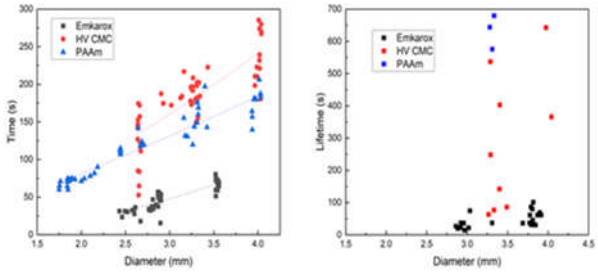
Objectives and stakes :

This research project aims at experimental investigation in transparent fluids to better understand fundamental mechanisms governing the formation, spreading and coalescence of bubbles or drops whether in a liquid or at a solid surface. Questions concerning the behavior and mechanisms of such bubbles and droplets composed in/with various fluids, such as their formations/coalescence in various phases/thinning behavior/ spreading on interfaces, etc., will be studied.

Methodology :

Rheological experiments for all working fluids were conducted with steady shearing method aiming to study the viscosity evolution. Bubble rupture and droplet coalescence processes were studied with a Newtonian fluid Emkarox and non-Newtonian fluid Polyacrylamide (PAAm), and high viscosity Carboxymethyl cellulose (CMC). Super-hydrophobic particles (Lycopodium, size of 30-40 um) were added on top of the air-liquid interface as covering or interphase layer. The speed fields were measured around the bubbles and droplets while their rupture and coalescence occur using PIV system with revised laser-fluorescent photo system (Developed by Prof. Li and PhD. Q. Zhang). By deriving these velocity fields, one can obtain the stress fields for the shear stress exerted by surrounding liquid. Analysis of the lifetime and rupture behaviors of bubbles could help understand the effect of fluid viscosity, particle packing density and thickness on the bubble behavior during the rupture process.

Illustration : Lifetime of bubbles. Left: bubble lifetimes in different fluids; Right: bubble lifetimes in different fluids under particle-laden air-liquid surface.



Main results

The layer of hydrophobic particles completely changed the bubble rupture process on air-liquid surface. Three typical behaviors: rapid breakup, slow shrink and fast shrink were detected via high speed camera observation. The main factors inducing behavior changes are particle layer thickness and fluid properties. Bubble lifetime are largely extended when particles were added on the surface. Increasing particle density and layer thickness, along with the duration of particle layer upon liquid surface could increase lifetime of bubbles. Higher viscoelasticity significantly increased the strength of bubble sphere, which, at a great chance, leads to partial rupture resulting a fast-shrinking bubble, and finally a non-rupture slow-shrinking bubble. Lifetime for PAAm bubbles increased 2.5 times when CMC and Emkarox bubble only increased 0.3-1 times compared with bubbles on particle free surfaces. Velocity fields derived from PIV images indicate transformation of underwater flow fields for bubble rupture process. Eddies detected are results of regrouping of particles on surface.

References :

[1] D. F. Evans and H. Wennerström, Colloidal Domain (VCH Publishers, New York, 1994).

[2] A. Saboni, C. Gourdon, and A. K. Chesters, J. Colloid Interface Sci. 175, 27 (1995).

[3] Q.D. Zhang *et al.*, Phys. Review E. 033112, 100(2019).

[4] J. Liu, C. Zhu, et al., Chem. Eng. Sci. 55-56, 93(2013).

2022

Research subject: Large-scale constructed wetlands : Monitoring and modelling

Nicolas Maurice (4th year)

Marie-Noëlle Pons, Nouceiba Adouani

Axe PERSEVAL

Keywords : constructed wetland, phytopurification, wastewater treatment plant, urban runoff, pollutants, modelling

General context, scientific issues :

Constructed at the output of wastewater treatment plants, artificial wetlands are used as a complementary way of protecting natural environments from pollutants, in addition to the abatement achieved by wastewater treatment plants. Furthermore, these wetlands could be a solution for treating urban wastewater bypassed during rainy events.

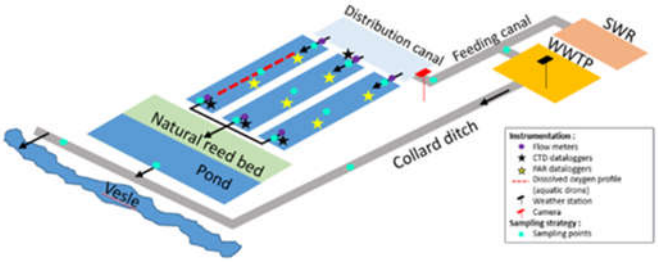
Objectives and stakes :

The construction of wetlands to polish the treatment of treated waters is already used in France, but it concerns small wastewater treatment plants. The purpose of AZHUREV project is to build a large-scale demonstration wetland downstream of the Grand Reims wastewater treatment plant to provide an improved treatment during dry weather and a treatment of bypassed stormwater. At the same time, this project aims to create habitats for wetland biodiversity. The first part of my thesis is to monitor the system and its performance, via sampling campaigns, in terms of abatement of primary pollution, organic and inorganic micropollutants, antibiotic resistant bacteria and faecal coliforms for dry and rainy weather conditions and to understand the abatement mechanisms. The second part is to model the constructed wetland with ordinary differential equations using MATLAB software and to verify the predicted results by comparison with recorded data.

Methodology :

The wetland is composed of three ponds (2 hectares), each with different types of macrophytes and vegetation in various amounts. By dry weather, a percentage of the water treated by the treatment plant is diverted and supplies equally each pond. During rainy events, the ponds are supplied by bypassed urban rainwater. Flow meters and temperature/conductivity sensors are installed at the entrance and exit of each pond on a hourly and 15-min basis, respectively. In each pond, two PAR sensors are set up in and measure a data every hour. A weather station measures air temperature, wind speed and direction, precipitations and PAR.

Illustration : Constructed wetland configuration and sampling points .



In 2019, a camera has been installed at the entrance to the wetland to monitor the development of vegetation. A sampling campaign of surface water is conducted monthly (see illustration). With an aquatic drone, water samples are collected in the ponds and dissolved oxygen and temperature are measured. For each season, sediments and aquatic plants are also sampled.

Parameters measured in water samples are : organic and inorganic carbon, total nitrogen and its most common forms, o-phosphates, chlorides, sulphates, Ca, K, Mg, Na, Si, trace elements, optical characteristics of organic matter, antibiotic resistant gene (class 1 integron), faecal coliforms and some organic micropollutants (pharmaceuticals, phthalates, AMPA, etc.)

Parameters to measure in plant and sediment samples are : Ca, K, Mg, Na, Si, trace elements and some organic micropollutants.

Main results

Removal of nitrogen (average efficiency = 50 %) by nitrification/denitrification, plants uptake and sediment adsorption.

Enrichment in dissolved organic carbon (average efficiency = -33%) and in phosphorus (average efficiency = -35%) by plant decomposition.

Removal of biodegradable and photodegradable pharmaceuticals.

References :

[1] Scholz & Lee (2005). Constructed wetlands: a review. *International journal of environmental studies*, 62(4), 421-447.

[2] Hantush *et al.* (2013). Nutrient dynamics in flooded wetlands. I: model development. *Journal of Hydrologic Engineering*, 18(12), 1709-1723.

[3] Vymazal (2007). Removal of nutrients in various types of constructed wetlands. *Science of the total environment*, 380(1-3), 48-65.

2022

Research subject: Metal recovery by agromining in French Guiana

Thomas Monot (1st year)

Baptiste Laubie, Marie-Odile Simmonot

Axe PERSEVAL

Keywords : Agromining; Gold; FPXRF; ICP-OES;

General context, scientific issues :

Agromining is the process of extracting metals with plants called hyperaccumulators able to store large amounts of said metals in some of their parts. Initially developed to extract nickel and rare earth elements, its potential is now being investigated for other elements. Gold agromining in French Guiana is of particular interest. Field trials have shown that gold hyperaccumulation can be artificially induced in plants, but no gold hyperaccumulator has ever been identified in its natural environment. This could be due to the lack of effective analytical tools able to perform plant elemental analysis on the field. Field Portable X Ray Fluorescence (FPXRF) spectrometers have shown a strong potential to fill this gap, thanks to their portable nature, ability to provide fast results and being non–destructive. Identification of gold hyperaccumulators in French Guiana could lead to the development of gold agromining in the region.

Objectives and stakes :

The first objective of this work is to determine whether a NITON FPXRF spectrometer is able to detect and accurately quantify gold in plants or plant ashes, with minimum sample preparation prior to analysis.

Methodology :

Synthetic gold standards with concentration ranging from 10 to 1000 ppm were prepared using microcrystalline cellulose and ashes from industrial oven by addition a chloroauric acid solution. These two matrices were chosen to simulate realistic hyperaccumulator samples both before and after the combustion step of the metal recovery process. Analysis were then carried out with a NITON xl3t GOLDD FPXRF spectrometer using two different modes: AllGeo mode and Soil mode. The standards were subsequently digested in aqua regia and analyzed by ICP-OES, and the results were compared with the ones returned by FPXRF. Finally, real ash samples from plants collected on gold-bearing sites in French Guiana were analyzed by both FPXRF and ICP-OES.

Illustration : Analysis using a FPXRF spectrometer

Main results

Comparison between the FPXRF and ICP-OES results showed that the NITON xl3t GOLDD was able to accurately quantify gold in both microcrystalline cellulose and ashes at concentration above 50 ppm in AllGeo mode. In Soil mode, gold was poorly quantified in ash synthetic standard. Gold was also detected in blank ash samples (with no gold added), and ICP-OES analysis revealed this to be a false-positive. We emit the hypothesis that this result might be caused by an interference with zinc, present in significant amounts in industrial oven ashes (around 240 ppm). Indeed, there is a possible overlap between emission ray of gold and zinc. This phenomenon was not observed with microcrystalline cellulose which does not contain zinc. Analysis of the French Guiana samples yielded similar results to industrial ashes: gold was detected in some of them in Soil mode while ICP-OES analysis indicated these results were false positives. These samples also contained zinc in variable amounts, strengthening our hypothesis about zinc interfering with gold detection. Therefore, FPXRF might not be best suited for gold detection in hyperaccumulators.

References :

[1] Anderson, C.; Moreno, F.; Meech, J. A Field Demonstration of Gold Phytoextraction Technology. *Miner. Eng.* **2005**, *18* (4), 385–392.

[2] van der Ent, A.; Echevarria, G.; Pollard, A. J.; Erskine, P. D. X-Ray Fluorescence Ionomics of Herbarium Collections. *Sci. Rep.* **2019**, *9*, 4746.

2022	**Research subject: : Determination of the reaction mechanisms involved in an organic dust explosion**	
	Matteo Pietraccini (3rd Year) Olivier Dufaud, Pierre-Alexandre Glaude, Anthony Dufour Axe PERSEVAL	

Keywords : pyrolysis, combustion, dust explosion, organic powders, reaction mechanisms

General context, scientific issues :

The importance of merging process safety and engineering design together is well known. However, for dust explosion as for other risks, the industrial conditions are multiple, changing and can hardly be reproduced in a laboratory by a series of experiments. Supporting the tests with a numerical model able to extrapolate their results to operating conditions other than those defined by the international standards, would increase the relevance of a normative approach.

Objectives and stakes :

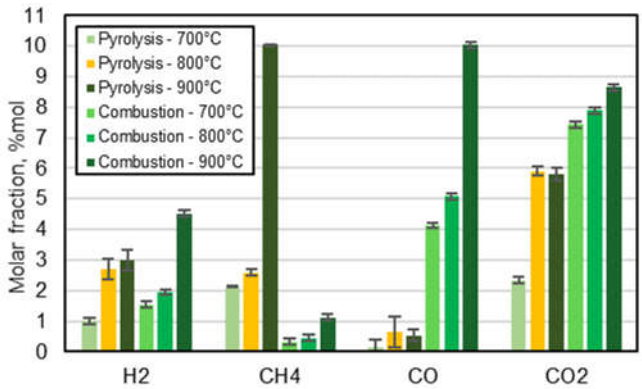
In order to model a dust explosion phenomenon, a gasification or a pyrolysis process, it is compulsory to determine the rate-limiting mechanisms occurring during the rapid heating of a dust cloud, followed by a flash pyrolysis and an oxidation step. Among the essential bricks of this model, the chemical reaction kinetics is probably the most central input. Unfortunately, at present, the proposed reaction mechanisms do not allow to represent the complexity of these phenomena, as they are almost always based on slow heating tests. The main goal of this work is to identify 5-10 lumped reactions able to coherently describe the kinetics of these phenomena.

Developing such a model is far from being easy as various steps have to be considered: the dust dispersion and its potential variation of particle size distribution, the dust ignition, which is by nature a discontinuous process, the flame propagation and the turbulence/combustion interactions.

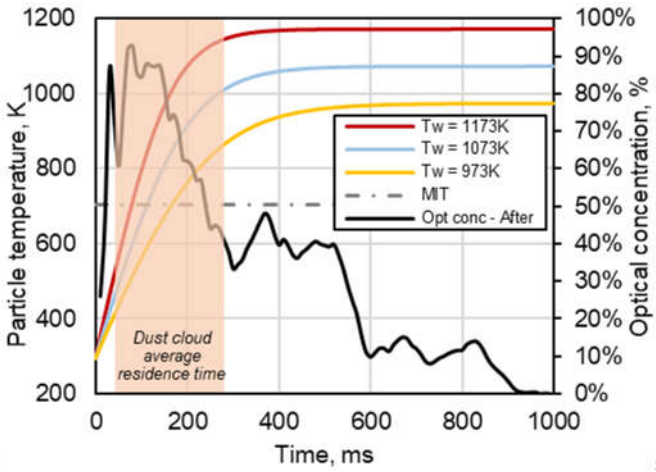
Methodology :

Cellulose was chosen as dust sample, since its chemical structure is well known. Its pyrolysis and combustion mechanisms were studied using a modified Godbert-Greenwald furnace, to reproduce the characteristics of a dust explosion. Average residence time and distribution were also estimated. Tests were performed at three different temperatures (700, 800 and 900°C). Gaseous products, solid residues and condensable molecules were sampled after the heated chamber, in order to obtain further information about the global conversion degree of the dust cloud.

Illustration : Permanent gas composition from flash pyrolysis and combustion tests



Dust cloud thermal study, combining an experimental and a modelling approach



Main results

Results showed a clear abundance in CH_4, H_2, CO and CO_2. The general reactions chosen for the model are:

Cellulose → Gases

Cellulose → Condensable molecules à Gases

Cellulose à Char + Gases

The Matlab code is currently being perfectionated. Data were introduced in an already existent model (realized by D. Torrado and A. Santandrea) in order to calculate the unstretched flame speed of cellulose, which seems to lay around 21.5 cm/s.

References :

[Santandrea, A. (2020). Process Safety and Environmental Protection, 134: 247–259.

Torrado, D. (2018). Process Safety and Environmental Protection, 118: 211-226.

2022

Research subject: Membrane process development to minimize environmental impacts of nickel recovery by agromining

Thomas Porqueddu (1st year)

Baptiste Laubie, Marie-Odile Simmonot

Axe PERSEVAL

Keywords : hydrometallurgy, Membrane processes, separation, Nickel, Ion transport modelling, speciation

General context, scientific issues :

This work falls within the context of the agromining chain, which aims to recover metals extracted from soils using plants. The objective is to improve the separation of metals of interest (in this case, Mg, Ni and Mn) contained in acid leachate obtained from plant ash using membrane processes. The aim is also to limit the consumption of reagents by recycling the acid. Membrane technology was chosen because it is known to reduce the environmental impact of industrial processes, especially if they involve many chemicals. It also offers high selectivity in the separation of metals, but the choice of best operating conditions depends very much on the speciation of the leachate.

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

Objectives and stakes :

The objective is to experimentally study the membrane separation of dissolved metals in highly acidic solution and to build a mathematical model to predict ion transport in nanofiltration membranes.

Methodology :

After a bibliographical study, nanofiltration experiments with model synthetic solutions (sulphuric acid + a dissolved metal) are carried out, in order to obtain data for the validation of the calculation code.

In parallel, a mathematical model of electromigration diffusion solution (SDEM), based on the Nernst equation, is being written in MATLAB. For the moment, it is adapted to three ions and will be completed by taking speciation into account, by coupling it to PhreeqC

Metal separation can be performed using nanofiltration, because this type of membrane allows the monovalent ion to pass, but not the divalent one. However, it will not be effective in achieving separation of divalent metals. Some technology, such as ultrafiltration assisted by complexation or shear-induced ultrafiltration assisted by complexation will be explored.

Illustration : **:** nanofiltration pilot

Main results

The first nanofiltration experiments (acid solution + Ni) showed that it was possible to concentrate each metal, up to a retention factor of over 90% for Ni. This is possible thanks to the recent development of new membranes that can be used in very acidic environments.

The mathematical model was able to reproduce this result, the adjustable parameter being the permeance. For those carried out with Mn and Mg, the results are currently being acquired.

In the short term, other experiments will be carried out with a mixture of several metals and later with a plant ash leachate.

The model is being generalized, with the aim of coupling it to the solution equilibrium calculation code PhreeqC.

In the longer term, this approach will be applied to other industrial leachates and should lead to improved separations with substantial chemical savings. The knowledge acquired will be fundamental for the recycling of metals by hydrometallurgy, a field that is growing rapidly due to the scarcity of mineral resources.

References :

J. Lopez, A. Yaroshchuk, M. Reig, O. Gibert, J.L. Cortina (2021) An engineering model for solute transport in semi-aromatic polymeric nanofiltration membranes: Extension of Solution-Electro-Diffusion model to complex mixtures, Journal of Environmental Chemical Engineering, Volume 9, Issue 4

2022

Research subject: Airflow Computational Simulation in Pleated Filters to Study the influence of Solid Volume Fraction Heterogeneities

Aishwarya Singh Rathore (Ingénieur d'Études)

Nathalie Bardin-Monnier, Augustin Charvet

Axe PERSEVAL

Keywords : Pleated Filters, Heterogeneities, Solid Volume Fraction (SVF), Permeability (K), Computational Fluid Dynamics (CFD)

General context, scientific issues :

Air pollution, due to high concentrations of fine/ultrafine particles, was ranked as the leading cause of death in the world, in a recent report by the State of Global Air, 2018. The efficient fiber filtration process, for this fine particle separation, encounters great difficulties of clogging due to a significant increase in pressure drop resulting from the higher specific surface area of particles. To delay the onset of clogging, the surface area of fiber filters is increased through the pleated process. However, this method of manufacturing generates local solid volume fraction heterogeneities. This filter characteristic being the critical parameter affecting the filter performance, it is essential to know the impacts of such modifications on the structure of a filter.

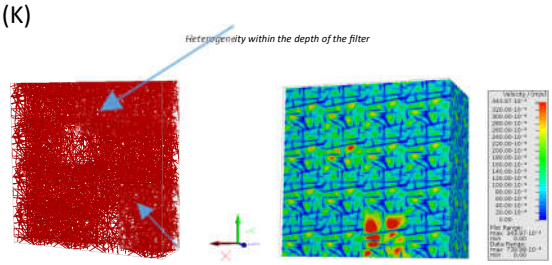
Objectives and stakes :

To study the impact of solid volume fraction heterogeneities on the overall performance of filters, the available experimental technique allows access to very localized information. Hence the CFD approach is adopted to perform the detailed study using the software, GeoDict. The characterization of the impact of the pleating processes is done to optimize the shape and angle of the pleats. The objective is thus to either limit heterogeneities if they degrade the performance of pleated filters, or to promote them up to a certain limit if they prove to be beneficial.

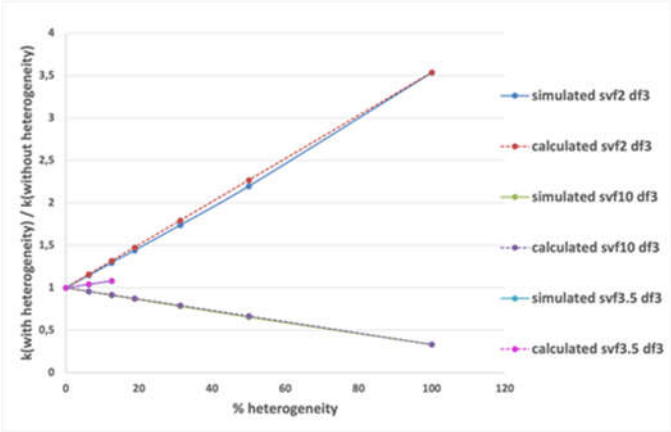
Methodology :

In addition to heterogeneities on the surface, and the thickness of the media, pleated filters present gradients of SVF in the depth of the fold as well, specifically at the bottom due to the pleating process implemented. Hence, the approach determines the filter permeability and efficiency of 3D fibrous structures with added heterogeneities generated on GeoDict. The progress made so far consists of performing a CFD simulation of a 3D fibrous structure made with fixed structural parameters like fiber diameter, size distribution, etc., with added heterogeneities in the form of different SVF. An analytical model for calculating K in the presence of heterogeneity was also used, to compare the calculated and simulated values of K. The influence of heterogeneity location within the homogeneous domain is also discussed.

Illustration : Effect of added SVF heterogeneity on filter permeability (K)



Fibrous Structure and its flow visualization with two lower SVF heterogeneities within the depth of the filter



k (with heterogeneity) / k(without heterogeneity) with respect to % heterogeneity in the homogeneous domain for one random seed, the fibre diameter of 3mm, and heterogeneity SVF as 2% and 10%

Main results

The filter manufacturers can be advised based on the following results for monolayer media as the cautions to be considered while processing:

Insignificant difference (≤1%) between the calculated and simulated K.

With less % (≤12%) of heterogeneity within the homogeneous domain, the effect of different values of SVF on K is not significant.

For lower SVF heterogeneity, the K increases with an increase in its % within the homogeneous domain. Vice versa for higher SVF heterogeneity.

No significant impact on K of changing the location of heterogeneity within the domain.

K increases when the heterogeneities are located one after another within the depth of the filter, then when distributed randomly.

Further steps include performing the efficiency study for each of the simulated cases for effect on K.

References :

1. Aerosol Filtration, D. Thomas, A. Charvet, N. Bardin-Monnier, J. Christophe Appert-Collin, 2017.

2022

Research subject: Wastewater treatment using novel electro-mixing reactor – comparison with conventional filter press electrochemical reactor

Kevin Roudaut (Research Engineer)

Nouceiba Adouani, Eric Olmos

Axe PERSEVAL

Keywords : Electrochemical advanced oxidation, electro-mixing reactor, microfluidic thin film, wastewater treatment, water reuse

General context, scientific issues :

In power plants, important quantities of energy are generated through physical reactions (combustion, nuclear fission). Therefore, effective cooling systems are needed to evacuate heat excess.

In France, half closed systems are mainly used. Those systems use cooling towers and have an important need in water, partly due to evaporation loss. To address it, water is collected from natural sources, usually rivers.

Inside those systems, especially in the condensers, Fouling and Biofouling result of the operating conditions. Biofouling results from microorganism development. Indeed, suitable temperatures (25-45°C), organically charged water allow good biofilm growth conditions.

However, the thickness of biofilms reduces significantly the efficiency of the heat transfer. Furthermore, biofouling can cause biological pollution, corrosion. Also, the cleaning processes to remove biofilms causes chemical pollution.

Objectives and stakes :

- With a laboratory pilote, identify experimental conditions allowing the lowest biofouling (biofilm thickness).

- Use the results to design a mathematical model coupling biofouling development (including the kinetics of growth, death and detachment), heat and mass transports and hydrodynamics.

- Determinate the impact of those phenomenon and their inter-connexion and in particular, the effect of biofouling on the efficiency of the cooling process.

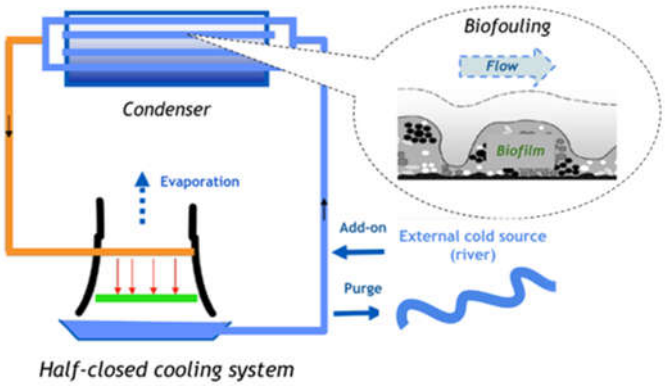
Methodology :

A laboratory pilote was designed to reproduce large operative conditions of actual industrial heat exchangers used in power plants.

Based on an experimental design, natural water collected from different rivers, heated at different temperatures, will flow under several hydrodynamic conditions (fluid velocity, turbulence regime, shear stressing).

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 and will be analysed with microscopic and metagenomical techniques.

Illustration : Representation of the scientific issue



Perspectives

The expected results should allow creating a model able to optimize the cooling process, predicting biofilm development and thermal efficiency loss and adapting the settings (flow rates, shear stress, temperature) to reduce this impact. It could also be used to determine the threshold of interference of biofouling to reduce biocides use and then rivers pollution.

The model should also be transposable to different types of heat exchangers integrating different qualities of water (chemical and biological). It should also be used as an ultimate purpose to design new heat exchangers with limited biofouling impact.

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.

2022

Research subject: Dust explosion modeling: application to organic/mineral powder mixtures

José Serrano (1st year)

Olivier Dufaud, Laurent Perrin

Axe PERSEVAL | TECALIMAN

Keywords : dust explosion, ATEX, powder mixtures, animal feed industry, process safety, risk assessment, modeling, combustion products

General context, scientific issues :

The explosion risk assessment related to combustible dust is based on the determination of the likelihood of dust dispersion, the identification of potential ignition sources, and the assessment of the explosion consequences. Within this context, adding mineral particles to combustible powders can significantly impact all these steps [1]. Several industrial applications exist for such mixtures of combustible and inert powders, from the pharmaceutical to the nuclear industries [2]. The animal feed industry is no exception, and the use of "premixes" combining combustible organic materials (e.g., cereals) and minerals (e.g., calcium carbonate) is widespread. However, there is no predictive model for estimating the safety parameters of such mixtures [1,2], and the risk assessment relies upon present on the multiplication of standardized tests to provide the necessary safety [2]

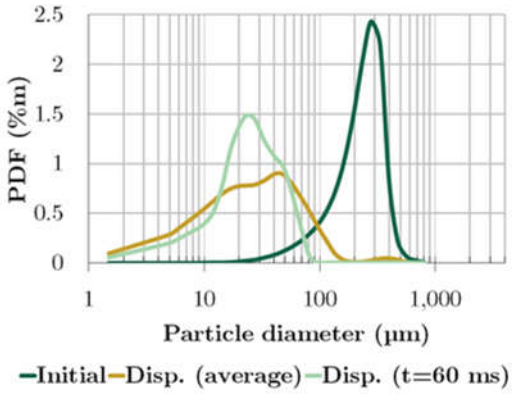
Objectives and stakes :

The scope of this research program is to consider the physicochemical contributions of mineral additives to propose predictive models to assess the ignition sensitivity and explosion severity (Kst) of organic and mineral powder mixtures used for the manufacturing of premixes in the animal feed industry.

Methodology :

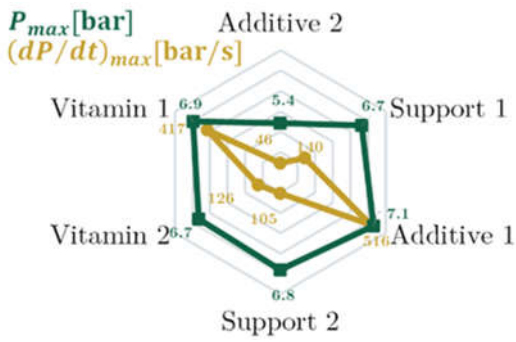
According to the applications identified by TECALIMAN and the industrial partners involved, this project aims to highlight and quantify the influences of the particle size distributions (PSD), powders proportions, fuel equivalence ratio, and powder chemical nature on the explosion risk of dust mixtures. An extensive parametric study will be conducted using the modified Hartman Tube (Minimum Ignition Energy) and the 20L Siwek sphere (Kst) based on the 14034 and 13821 European Standard series. In addition, the composition of the combustion gases will be determined to assess the gaseous products generated by accidental combustion. Afterward, the models will be developed and adjusted according to the significant effects observed during the experimental tests and their future applicability to the development of intrinsically safer industrial processes.

Illustration : *Variation of the PSD due to the 20L sphere dispersion step of a vitamin product*



Main results

The above figure shows the PSD variation of a vitamin powder before (initial) and after its dispersion within the 20L sphere. The mean diameter at the ignition zone is about 10% of the corresponding value of the dust sample, which evidences the significant fragmentation due to the dispersion stage of the standard explosion test. The PSD also evolves with time, and both this parameter and the ignition delay time (here 60 ms) have a relevant influence on the explosion performance. The below radar chart evidences a more significant difference in the explosion dynamics than thermodynamic performance between the vitamins, additives, and organic supports. The explosion performance of the binary and then more complex mixtures will be studied in further steps.



References :

[[1] Janès, A., Vignes, A., Dufaud, O., & Carson, D. (2014). Experimental investigation of the influence of inert solids on ignition sensitivity of organic powders.

[2] Amyotte, P. R., Pegg, M. J., & Khan, F. I. (2009). Application of inherent safety principles to dust explosion prevention and mitigation.

2022

Research subject: Comparative evaluation of the potential recovery of strategic metals (Co, Ni) from old mine tailings using (hydro-)metallurgy and agromining approaches

Samuel Teillaud (2nd year)

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

Axe PERSEVAL

Keywords : Mine tailings repurposing, Cobalt, Agromining, Metal extraction, Hydrometallurgy

General context, scientific issues :

Mine tailings represent apromising secondary source of Strategic & Critical Metals (SCM) (e.g., Co, Ni) because:

• they contain some amounts of valuable metals,

• they arealready excavated and finely ground.

The recovery of Co and Ni from mine tailings might be of interest to:

• allow a stable and secure supply by diversifying sources (**economical benefit**),

• limit their impact on the environment during long-term storage (**environmental benefit**).

Objectives and stakes :

World increasing demands and monopolies of foreign countries have encouraged countries to find economically reliable sources which contains Co and Ni. The former Cobalt Mining Camp (ON, Canada) appears to be a promising location for the recovery of Co (up to 3.5 wt%)[1] and Ni (up to 2.2 wt%)[1] still present in mine tailings (arsenides, sulfides and sulfoarsenides). The aim of this project is to **compare the performance of two pre-treatment routes to pre-concentrate Co and Ni prior to chemical leaching** to reduce operating costs related to the use of reagents. Pre-concentration pathways include:

i) **Metallurgical approach** – use of gravity and/or magnetic separation as well as flotation

ii) **Agromining approach** – use of hyperaccumulator plants

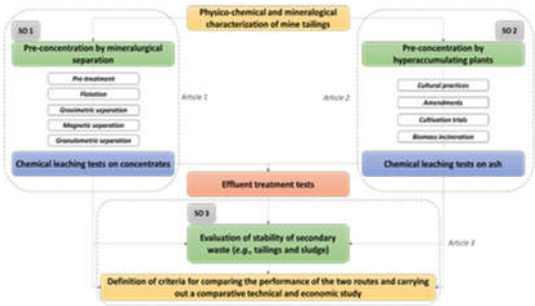
Methodology :

i) **Physico-chemical and mineralogical characterizations** of the tailings will be carried for the three different mine tailings.

ii) **Metallurgical processes** will be used to separate and pre-concentrate elements of interest using gravimetric/ magnetic separation, flotation. Subsequently, acid leaching tests (based on the previous characterizations and leaching tests and literature) will be performed on the pre-concentrated tailings.

iii) Performances of an **agromine system**, followed by the recovery of these elements from incineration ash of aerial parts of plants by chemical leaching will be also evaluated.

Illustration : General methodology .



iv) **Geochemical behaviour** of new solid and liquid releases generated by the different processes will be evaluated.

v) **Comparative study** of the efficiency of the two pathways (metallurgical and agromine) will be done to determine the most suitable reprocessing process pathway for the recovery of Co and Ni in these mine waste.

These two approachs will be compare according to different criteria (in terms of Co and Ni pre-concentration efficiency, amounts of valuable SCM recovered, stability of final residue and operating costs).

Main results

A consistent bibliographical synthesis has already been done. Furthermore, the three sites were selected in the former Cobalt mining camp. For example, at Site B, Co and Ni concentrations measured in situ by an X-ray fluorescence spectrometer range from 200 to 17,500 $mg.kg^{-1}$ for Co and 45 to 10,400 for Ni, with an average Co/Ni molar ratio of 2.3. For the processes, the results are currently being acquired .

References :

[1] Percival et *al.*, (2007) « Distribution of As, Ni and Co in Tailings and Surface Waters in the Cobalt Area, Ontario », Sudbury 2007 – Mining and the Environment International Conference

PRIMO

PROCESSES, REACTORS, INTENSIFICATION, MEMBRANES, OPTIMIZATION

LRGP
LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

2022

Research subject: CFD simulation of hydrodynamics and heat/mass transfer phenomena in membrane gas separation processes

Omar Abdul Majid (1st year)

Rainier Hreiz, Éric Favre

Axe PRIMO

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

General context, scientific issues :

Gas separation processes using membranes are gaining importance in industrial applications such as CO_2 capture, natural gas purification, etc., especially with the emergence of new inorganic materials offering high levels of selectivity and/or permeability [1].

However, high permeation fluxes may lead to mass transfer limitation within the gaseous mixture, i.e. concentration polarization phenomena. This effect is not accounted for existing 1D models [2] which calls into question their validity for predicting separation performance in such processes.

Objectives and stakes :

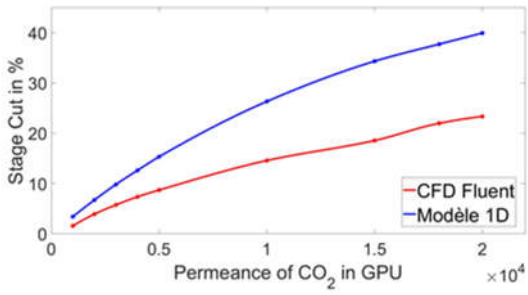
This PhD study aims at developing a full CFD model for simulating gas permeation in inorganic membranes. Comparison with the 1D modeling approaches used thus far in the literature [2] will allow identifying their limitations when applied to such processes

Methodology :

The commercial CFD code ANSYS Fluent is used for simulating the coupled transfer phenomena inside a tubular (hollow fiber) gas permeation membrane. Firstly, simulations are performed in the case of a pure gas and the numerical results are validated by comparison with the theoretical model of Berman [3]. Secondly, simulations are carried out for gas mixtures permeation in classical membranes and results are validated by comparison with those provided by the commercial code MEMSIC [2] which relies on a systemic 1D modeling approach.

Finally, experimental validation will be carried out by comparison with data found in the literature as well as with experimental results acquired on a high-performance inorganic membrane available at the LRGP laboratory. Once the CFD model is proven to be accurate, it will used to generate a general cartography for identifying the operating conditions where mass transfer limitation occurs within the gas phase. The calculation of a concentration polarization index will allow quantifying the amplitude and the effects of the phenomenon. .

Illustration : Permeance effects and polarization impact on the stage cut: CFD versus 1D modeling approaches



Main results

As explained before, and due to the axial symmetry in the hollow fiber membrane problem, a 2D CFD model to simulate the coupled transfer phenomena is done.

In the first comparison with the theoretical equations, the CFD model gave us the expected results with less than 1% of error.

Next, as shown in the illustration above, it is obvious that the CFD model do not overestimate the performance like the 1D simplified models, because it calculates the velocity, temperature, concentration profiles, … in every point of the domain especially the boundary layer due to finer meshing there.

Moreover, it allows us to identify the operating conditions leading to high polarization, by testing the parameters individually or in combination to illustrate what is occurring in the membrane module.

Finally, this model gives us the ability to calculate accurately the Sherwood number and evaluate correction factors, in order to improve the available mass transfer correlations under significant polarization of concentration conditions.

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] S. Karode, « Laminar flow in channels with porous walls, revisited », J. Membr. Sci., vol. 191, no 1–2, p. 237–241, sept. 2001, doi: 10.1016/S0376-7388(01)00546-4.

2022

Research subject: Study and development of design methods for multifunctional reactors coupling balanced exothermic chemical reaction, heat transfer and membrane separation

Chakib Rafik Behloul (3rd year)

Pr. Jean-Marc Commenge, Pr. Christophe Castel

Axe PRIMO

Keywords : Process intensification, Process design, Multifunctional reactor, Catalytic reactor, Heat exchanger, Membrane separation, Optimization, Modeling, Power-to-X, CO_2 valorization, Renewable H_2, dimethyl ether (DME), Transfer phenomena.

General context, scientific issues :

In addition to CCS technologies, decarbonated energy sources in industry sectors (low-carbon energy) and process efficiency improvement are becoming a necessity. These evolutions intend to meet the net zero carbon objective at the 2050 horizon, while creating economic wealth simultaneously. Nowadays, the energy transition requires the development of processes and technologies for a resource and energy efficient process industry. In this context, the Power-to-X concept, as a sector coupling and energy storage technology, has been the subject of intense discussion in recent years for an integrated future energy system architecture. This concept enables the synthesis of high value-added products for several purposes (alternative fuel, petrochemical feedstock, etc.) through the CO_2 hydrogenation reaction.

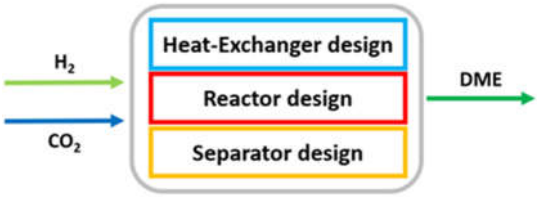
Objectives and stakes :

The current energy transition requires that certain raw material and energy transformation processes should be partially modified or deeply redesigned to meet more sustainable operating conditions (electrification of unit operations, intermittent operation, decentralized production, etc.). Process intensification enables the development of multifunctional units, which exploit the synergies between elementary processing functions (reactions, transfers, separations, etc.) within a single equipment, to reduce the energy impact of these processes. The integration of multiple functions within an equipment is a potential source of economic and energetic gains, especially when balanced exothermic reactions are intensified thanks to innovative coupling approaches. In this context, the dimethyl ether (DME), as alternative fuel, is expected to play an important role in the energy transition. The DME direct synthesis from captured CO_2 and renewable H_2 is considered, first as a case study, because its industrial synthesis has attracted attention in recent years due to its potential in different

Methodology :

The concept of multifunctional reactors, coupling several elementary functions, has been a real success when historical demonstrators were created (Eastman-Kodak process, …), but their implementation has not been generalized, due to a lack of practical design methodology. Therefore, the definition of innovative approaches helps to fill this methodological gap. The applied methodologies offer the possibility to explore a much wider range of degrees of freedom, enabling to reveal the maximum achievable performances, that further process design steps should try to reach. The developed methodologies in this work rely mainly on the dynamic optimization of the mass and heat flux profiles and on the characteristic time analysis and dimensionless numbers. The proposed methodologies enable to quantify the impact of couplings on the performance of the synthesis, with a view to targeting intensification strategies that will take advantage of their synergies. These methodologies can be extended and easily used for other balanced exothermic reactions (Methanol, Synthetic Natural Gas, etc.)

Illustration : Schematic view of proposed multifunctional reactor configuration.



Main results

Figure 2: Impact of characteristic time ratios on process improvement

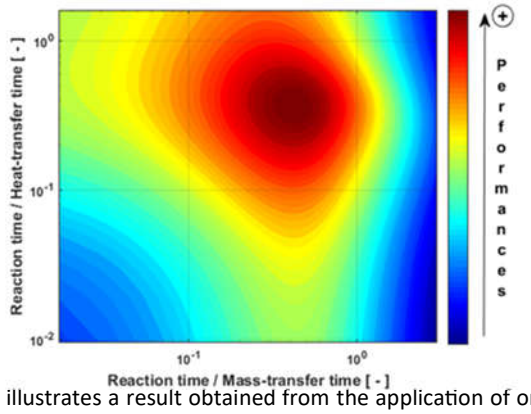


Figure 2 illustrates a result obtained from the application of one of the developed methodologies based on the characteristic times. The analysis of this result provides an overview of the rates characterizing each phenomenon. The results clearly reveal the requirement of a trade-off between these couplings in order to achieve optimal conditions (synergic effect).

References :

(1) Behloul, C. R.; Commenge, J.-M.; Castel, C. Simulation of Reactors under Different Thermal Regimes and Study of the Internal Diffusional Limitation in a Fixed-Bed Reactor for the Direct Synthesis of Dimethyl Ether from a CO_2-Rich Input Mixture and H_2, Ind. Eng. Chem. Res, 60 (4) (2021) 1602–1623

(2) Behloul, C. R.; Commenge, J.-M.; Castel, C. Influence of the synergy between reaction, heat exchange and membrane separation on the process intensification of the dimethyl ether direct synthesis from carbon dioxide and hydrogen. Chem. Eng. Pro. Process Intensification, 167 (2021) 108513

2022

Research subject: Development of catalysts for the production of hydrogen by dry reforming of biomethane.

Faicel Belgacem (1st year)

Laurent Falk, Jean-François Portha, Raphaël Schneider

Axe PRIMO

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

General context, scientific issues :

The challenges of new hydrogen synthesis routes are enormous. Dry methane reforming (DMR) is a reaction of interest which offers many environmental prospects by valorizing two greenhouse gases, CO2 and CH4, the main components of biogas. However, these molecules being very stable thermodynamically, the operating conditions for reacting them are extreme, requiring a very high temperature of the order of 700 to 1000° C at atmospheric pressure. Furthermore, the reaction is highly endothermic, which requires a significant heat input. The challenges encountered for the valorization of biogas by DMR lie in the energy efficiency of the process and the development of catalysts compatible with the use of milder conditions and allowing the minimization of coke deposition. This last point constitutes the main obstacle to its industrial application [1].

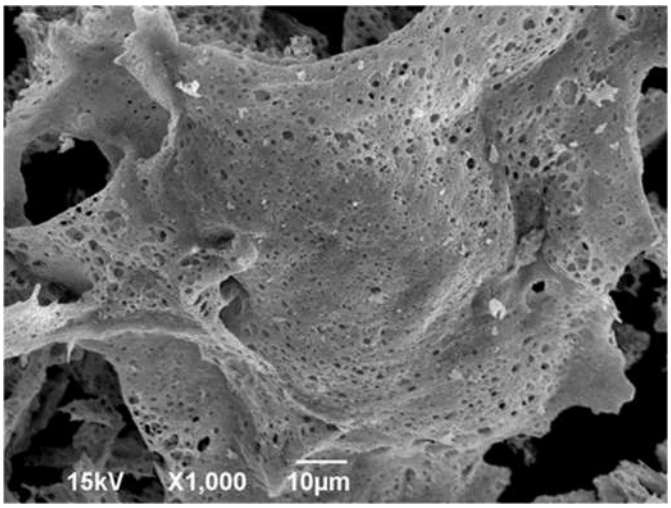
Objectives and stakes :

The objective of this work is to optimize the formulation of perovkites catalysts used in the DRM reaction as well as optimizing the operating conditions in a catalytic microreactor. Subsequently, the most efficient catalyst(s) will be selected for a kinetic study. Finally, models will be used to carry out a simulation of an industrial process.

Methodology :

Perovskites are ABO_3 type oxides. In catalysis, their reduction under dihydrogen allows the partial exsolution of metallic nanoparticles (B sites), which makes it possible to obtain supported nanoparticles highly dispersed on the surface of the perovskite as well as a strong metal-support interaction. In particular, they make it possible to oxidize the carbon deposited on the surface of thecatalyst, which makes them particularly interesting for the DRM reaction.The structure of perovskites makes it possible to modulate their compositions via the cations of sites A and B. This partial substitution allows the incorporation of different metals with oxidation-reduction properties to eliminate carbon deposited on the active metal [1].

Illustration : SEM image of fresh catalyst $SrZr_{0.25}(Ni_{4/5}Fe_{1/5})_{0.75}O_3$



Main results

Recent works on perovskites of formula $SrZr0_{.85}Fe_{0.03}Ni_{0.13}O_3$ led us to study the influence of different formulations, in particular the doping in Ni and/or Fe as well as the partial substitution of Sr by Ce to improve the properties. oxidation-reduction as well as to reduce the deposition of carbon and the sintering of the catalyst [2].

To do this and firstly, catalysts $SrZr_x(Ni_{4/5}Fe_{1/5})_{1-x}O_3$ type with x varying from 0 to 1 in steps of 0.25 were synthesized by the self-combustion and citrate method.

After screening the different samples, the catalyst with the best performance in terms of stability/yield will be selected for a second series of tests aimed at preparing catalysts of the $Sr_yCe_{1-y}Zr_x(Ni_{4/5}Fe_{1/5})O_3$ type with y varying from 0 to 1 in steps of 0.25.

In a third part, we will focus on the synthesis of perovskites supported $SrZr_x(Ni_{4/5}Fe_{1/5})O_3/CeO_2$, $Sr_yCe_{1-y}Ni_{4/5}Fe_{1/5}/ZrO_2$ and $SrNi_{4/5}Fe_{1/5}O_3/Ce_xZr_{1-x}O_2$. This study will determine the influence of Zr and Ce promoters in the perovskite structure and as supports.

References :

[1] Bhattar, Srikar; et al., Review on Dry Reforming of Methane over Perovskite Derived Catalysts, Catalysis Today, 2021, vol. 365, p. 2□23.

[3] Khazaal, Majida H.; et al., Enhanced Methane Reforming Activity of a Hydrothermally Synthesized Codoped Perovskite Catalyst, Energy & Fuels, 2018, vol. 32, no 12

2022

Research subject: Thermodynamic analysis of concentrated solutions of sulfuric and phosphoric acids in the presence of phosphate ore: modeling and experimentation

Ilias Bouchkira (Defended on April 24th 2022)

Abderrazak M. Latifi

Axe PRIMO

Keywords : Thermodynamics, Phosphate ore, phosphoric acid, Modeling, Simulation, Optimization

General context, scientific issues :

In the phosphate industry, phosphoric acid is a major component in the manufacture of fertilizers. It is mainly produced by the attack of phosphate ore with sulfuric acid. In the wet process, after its mining and beneficiation, the ore is fed to the digestion tank where it reacts with a mixture of sulfuric acid and phosphoric acid solutions. The phosphoric acid process has been, and continues to be the subject of many industrial and academic studies, at laboratory and pilot scale, and even at industrial scale **[1]**. However, although the phosphoric manufacturing process is widely studied in the literature, its design and mastering of its operation still pose several problems due in particular to the lack of thermodynamic, kinetic, hydrodynamic data ..., and to the lack of knowledge on many complex phenomena involved in the process. The understanding of these phenomena as well as accurate experimental measurements of the relevant variables are some of the key issues of the project that should be addressed in order to optimally design and operate the phosphoric acid processes

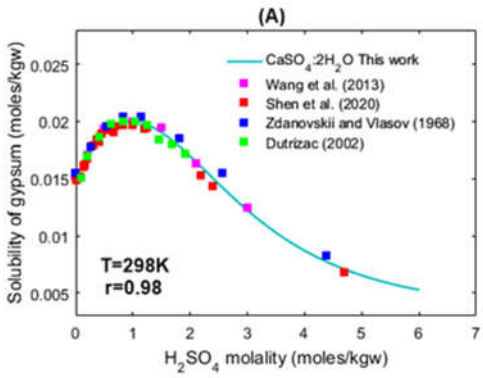
Objectives and stakes :

The objective of this work is the development of a database of physical and chemical properties of major subsystems involved in phosphoric acid processes. This is achieved by carrying out experimental measurements and thermodynamic modeling of vapor/liquid/solid equilibria.

Methodology :

Measurements of phase equilibria and physical properties of sulfuric and phosphoric acid solutions are carried out at the laboratory scale for different temperatures and concentrations. On the other hand, Pitzer's model **[2]** is used for thermodynamic modeling and involves several unknown parameters that should be deduced from the measurements. However, it is well admitted that all the unknown parameters cannot be estimated from the available measurements. In order to determine the set of the most estimable unknown parameters, an estimability analysis approach is developed based on the use of global sensitivities **[3]**.

Illustration : predicted gypsum solubility



The most estimable parameters are then identified using a branch-and-bound optimization algorithm and their accuracy is assessed by means of confidence intervals. The least estimable parameters are fixed from previous studies or from literature.

Main results

The developed models allow us to accurately predict important equilibrium parameters as well as physical properties of the acid solutions considered. Further development of these models will enable the prediction of important operating variables of industrial phosphoric acid processes, e.g. free sulfates concentration which impacts directly the yield of the phosphate ore attack, the gypsum saturation and also the phosphate losses. Furthermore, the developed models can be used and implemented within (multi-objective) optimization algorithms in order to improve the current operating conditions of phosphoric acid manufacturing processes.

References :

[1] Becker, P. (1983). Phosphates and phosphoric acid. Marcel Dekker, Inc..

[2] Pitzer, K. S. (2018). Activity Coefficients in Electrolyte Solutions: 0. CRC press.

[3] Bouchkira, I., Latifi, A. M., Khamar, L., & Benjelloun, S. (2021). Global sensitivity based estimability analysis for the parameter identification of Pitzer's thermodynamic model. Reliability Engineering & System Safety, 207, 107263.

2022

Research subject: Performance evaluation of pilot-scale reverse osmosis process

Janney Debleza (Research engineer)

Eric Favre[1], Christophe Castel[1], Thibault Neveux[2], Florian Moyano[2]

Axe PRIMO |EDF [2]

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

General context, scientific issues :

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

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

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

Objectives and stakes :

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

Methodology :

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

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

Illustration : Reverse osmosis unit

References :

[[1] Sasaki, Takao; Okabe, Jun; Henmi, Masahiro; Hayashi, Hiromasa; Iida, Yutaka (2013). Cesium (Cs) and strontium (Sr) removal as model materials in radioactive water by advanced reverse osmosis membrane. Desalination and Water Treatment, 51(7-9), 1672–1677.

[2] C. Fritzmann; J. Löwenberg; T. Wintgens; T. Melin (2007). State-of-the-art of reverse osmosis desalination. , 216(1-3), 1–76.

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

2022

Research subject: In situ kinetics measurement of catalysed dissolution: Application to the bioleaching of cobaltiferous pyrite

Clément Duval (1st year)

Eric Schaer, Anne-Gwénaëlle Guezennec, Alastair Magnaldo

Axe PRIMO

Keywords : Process Engineering, Dissolution, Bioleaching, Kinetics, Catalysis, Bacteria, Modeling, Pyrite

General context, scientific issues :

Leaching processes are widely used in the industry (e.g. mining industry, nuclear industry or food industry) and the study of the involved phenomena (transfer mechanisms, kinetics etc …) is complex to set up. Leaching reactors are multi-phase systems in which chemical reactions can be limited by transfer phenomena. Indeed, reactions kinetics depend on reagents concentrations, which are directly impacted by these transfer phenomena. Finally, the measured reaction kinetic is the addition of the duration of these several phenomena resulting in a potential false estimation of the real chemical kinetic. This last parameter is however essential in the understanding of leaching mechanisms and their extrapolation to industrial scale processes.

Leaching is for example the first step of hydrometallurgical processes. This step allows the dissolution of some solid species in solution as ions for further selective separations. Among leaching processes, bioleaching consists in a microbial assisted leaching through oxidation or reduction reactions enabling the regeneration of some reagents. This process can be operated at low costs due to the soft used conditions (T, P) and the low reagent consumption. Bioleaching can be used for the treatment of different kind of ores such as copper or gold ores [1]. Other studies focus on the development of this process for metal recycling [2]

Objectives and stakes :

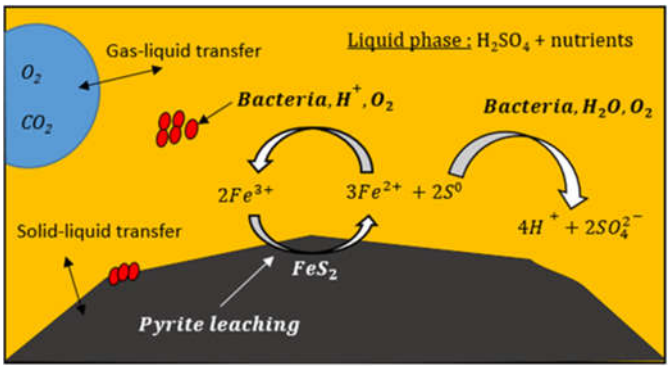
This study aims to develop a method allowing a direct access to the measurement of leaching kinetics in a catalyzed medium. This method should grant results that will not be limited by transfer phenomena or side reactions. A theoretical model will be developed from these results.

Methodology :

The kinetics study will rely on an optic device allowing the in situ observation of dissolving particles [3]. The used material of interest will be a cobaltiferous pyrite mineral. The observation will focus on pyrite bioleaching. The reaction will be set in a specific dissolution reactor enabling particles observation using ombroscopy principle. A camera will monitor particle size change over time. The images will be analysed to calculate the chemical kinetics.

Several key-parameters previously identified in literature [4,5] will be investigated in order to obtain a complete model of the involved mechanisms. Among them, reagent concentrations, pH and redOx potential can be mentioned

Illustration : Pyrite Bioleaching



Ongoing activities:

Preliminary experiments have been carried out in order to prepare the observation and the bioleaching set up (reactor residence time, thermal loss …) and anticipate negative effects on the kinetics measurements.

A microbial bioleaching consortium has been progressively adapted to the desired leaching conditions (pH, T, concentrations…).

Perspectives:

This project should grant a more accurate measurement of pyrite's bioleaching kinetics in controlled and stable operating conditions. It should also strengthen the knowledge of the related mechanisms.

This work also aims to develop a method adapted for the image treatment of a heterogeneous population of particles containing non-soluble elements.

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References :

[1] D.E. Rawlings, B.D. Johnson, D.E. Rawlings, Biomining, Springer, Berlin, 2007.

[2] A. Hubau, Conception d'un procédé de biolixiviation pour la valorisation des métaux contenus dans les déchets de cartes électroniques, (2019).

[3] F. Charlier, Réactions autocatalytiques hétérogènes: vers le dimensionnement des réacteurs industriels de dissolution du dioxyde d'uranium, (2018).

[4] F.K. Crundwell, Modeling, simulation, and optimization of bacterial leaching reactors, Biotechnology and Bio

2022

Research subject: Modeling, simulation, and experimentation of the digestion tank in a phosphoric acid manufacturing process

EL MISAOUI Sanae (4th year)

Abderrazak Latifi, Mohamed Salouhi (EMI, Maroc)

Axe PRIMO | PSE

Keywords : phosphoric acid manufacturing process, phosphate rock dissolution, digestion tank, modeling, simulation, optimization, experimentation

General context, scientific issues :

Phosphoric acid is a key product in many industrial applications, e.g., production of fertilizers, food, and even pharmaceutical industry. Its manufacturing process is one of the most important processes in phosphate industry [1]. The design and operation of these processes still pose several problems due to the lack of thermodynamic, kinetic, hydrodynamic data ..., and to the lack of knowledge on many complex phenomena involved in the process. It is therefore of utmost importance to understand these phenomena to accurately model and optimize the process performances in general, and the digestion tank in particular, which constitutes the heart of the process.

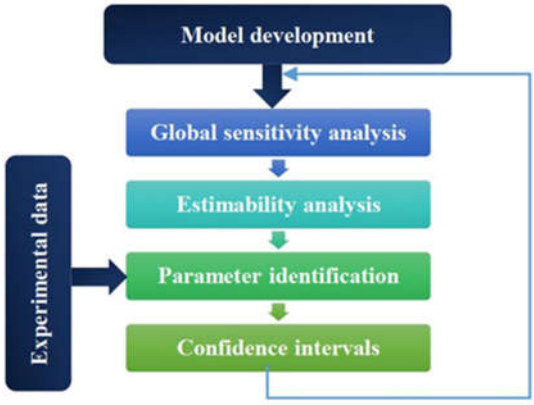
Objectives and stakes :

The objective of this work is to determine the optimal operating conditions that maximize the yield and purity of the phosphoric acid produced in the existing processes, and to design new compact, intensified, efficient and sustainable processes. The ultimate goal is to further value the phosphoric acid by broadening its fields of application and using it in the synthesis of products with very high added value.

Methodology :

The methodology adopted consists in developing accurate first-principles models in strong and permanent interactions with experimental measurements. The identified and validated models will then be used in optimal design and operation of processes. This work deals more specifically with the phenomena involved in the digestion tank, and more particularly with the dissolution of phosphate ore in a phosphoric acid, and the crystallization of the gypsum in the presence of the sulfuric acid solution. The dissolution of phosphates is considered as a non-catalytic liquid-solid with elimination of products [2]. However, the rate limiting step is not easy to determine. For this reason, an experimental approach to study the kinetics of the dissolution mechanism, including the identification of the limiting step is carried out. Furthermore, a crystallization model in developed by considering the nucleation and the growth phenomena

Illustration : Diagram of the phenomenological modeling approach



A global model is obtained by performing a coupling approach of the dissolution and crystallization models. The model obtained allows to describe in a satisfactory way the majority of the complex phenomena involved in the digestion tank.

Main results

Simulations are carried out using gPROMS software. The developed model predicted the concentration profiles in the liquid film surrounding the phosphate particles and in the liquid bulk within the digestion tank, the conversion rate by the dissolution step, and the nucleation rate, the growth rate, the supersaturation ratio, and the crystal size distributions, by the crystallization step. Statistical methods, static and dynamic data reconciliation, optimal experimental design, global estimability analysis are developed to identify the unknown parameters of the model from the available measurements (illustration1). The model outputs are compared to the experimental measurements. Once the final developed model is obtained, it will then be used to determine the optimal operating conditions that improve the performances of the existing phosphoric acid manufacturing processes .

References :

[1] P. Becker, *Phosphates, and phosphoric acid: raw materials, technology, and economics of the wet process*, 1983.

[2] *S. Van der Sluis, Y. Meszaros, W. G. J. Marchee, H. A. Wesselingh, and G. M. Van Rosmalen, 1987, The digestion of phosphate ore in phosphoric acid, Industrial & Engineering Chemistry Research, 26, 12, 2501-2505.*

2022

Research subject: C2FUEL : Carbon Captured Fuel and Energy Carriers for an intensified Steel Off Gases based Electricity Generation in a Smarter Industrial Ecosystem

Eglé Ferreri (Research Engineer)

Eric Favre, Christophe Castel

Axe PRIMO

Keywords : Membrane contactor, Carbon Capture and Storage (CCS), CO_2 capture, Chemical absorption, Power plant, Modelling and simulation, Pilot plant, Post-combustion, Process intensification

General context, scientific issues :

C2FUEL project aims to develop energy-efficient, economically and environmentally viable CO2 conversion technologies for the displacement of fossils fuels emission. This concept will be demonstrated at Dunkirk at DK6 power plant.

Main goal is to develop, integrate and validate processes at industrial-relevant scale, for the conversion of captured CO_2 from carbon-intensive industries off-gases, in formic acid and DME. The produced fuel will be tested locally, for transport through maritime/truck shuttle and green electricity transport and storage

Illustration : Mobile pilot unit installed in Dunkirk.

Objectives and stakes :

CO_2 present in flue gas (blast furnace gas) produced by Arcelor Mittal steel factor and routed to DK6 power plant, needs to be selectively captured, purified and sent in catalytic reactors. Purity requirement is high and will be achieved by implementing a chemical absorption process using hollow fiber membrane contactors (**HFMC**). HFMC consist in a gas-liquid contactor where hollow fibers act as an interface between the flue gas and the absorption solvent.

LRGP has been involved in numerous projects in this field: CICADI[1] and AMELIE[2] validated the concept of membrane contactor for CO_2 absorption at the lab scale on key chemical solvents; EnergiCapt[3] and C2B[4] projects involved the upscaling and its validation on real flue gas. Results shown in each case high intensification potential compared to conventional contactor. Thanks to its expertise, LRGP is responsible of developing a carbon capture and conditioning demonstrator unit for C2FUEL, able to produce 0.5 Nm^3/hr of CO_2 for 4,000hr.

Methodology :

LRGP contribution consist of 4 steps:

(i) Development of a lab-scale CO_2 absorption unit used to assess compatibility and performances of a selection of absorption solvents and several HFMC; (ii) Design, construction and commissioning of a fully instrumented mobile semi-industrial absorption and regeneration pilot plant, in order to assess impacts of real flue gas complex composition; (iii) Validation of an *ab initio* tailor-made 1D isothermal model of CO_2 chemical absorption by experimental results, to provide final design of the demonstrator unit; (iv) Design of a CO2 capture demonstrator according to experiments and modelling.

Main results

(i) A method has been developed to assess, through one experiment, both thermodynamics and mass transfer data based on a batch to continuous approach. The set-up can easily be used for studies of membrane and solvent performances, and allowed to obtain quickly key data of several solvents (MEA, MDEA, AMP, taurate) and commercial HFMCs. This work was presented during *Euromembrane 2021* and *ECCE/ECAB 2021*.

(ii) On site experimental campaigns with the mobile pilot unit have proven the effectiveness of a polymethypentene HFMC and MEA solvent with real flue gas over several hundred hours. Key pre-treatment technologies for removal of sulphur compounds and dust were also validated by attaining CO_2 purity and trace compounds requirements.

(iii) Both lab-scale and pilot-scale unit results were correctly predicted by a 1D absorption model.

(iv) Design and safety analysis of the demonstrator unit were performed, and construction by the manufacturer PIGNAT SAS is starting in June 2022.

References :

[1] Chabanon, Roizard, et Favre, « Membrane Contactors for Postcombustion Carbon Dioxide Capture»

[2] Makhloufi et al., « Ammonia Based CO2 Capture Process Using Hollow Fiber Membrane Contactors »

[3] « Projet CO2 EnergiCapt »

[4] « Projet C2B »

2022

Research subject: Analysis and quantification of catalyst deactivation during acrolein synthesis by propylene oxidation for the manufacturing of nutritional additives

Karima Gahfif (4th year)

Éric Schaer, Jean-François Portha

Axe PRIMO | Adisséo

Keywords : : heterogeneous gas/solid reactions, catalyst deactivation, experimental characterization, reactor modeling, intensification

General context, scientific issues :

The manufacturing of methionine, an animal feed additive, requires the catalytic oxidation of propylene to acrolein. This highly exothermic reaction has been the subject of numerous studies [1][2]. The results show that the secondary reactions are thermally activated and that any deviation from an optimal temperature profile induces the formation of hot spots that negatively affect acrolein yield and selectivity. Furthermore, these hot spots promote the formation of by-products, some of which have a bad effect on catalyst activity. The parasitic reactions lead to more than 40 lights or fouling side products causing frequent shutdowns of the industrial reactor which, added to low propylene yields, increase operating costs

Objectives and stakes :

The aim of this thesis is to develop a global model of the industrial acrolein production reactor taking into account catalyst deactivation. The ultimate goal will be to optimize the operating conditions to extend the catalyst life while maintaining the desired value of acrolein yield

Methodology :

The first step of this work is to establish a kinetic model without considering the deactivation effectA kinetic model is developed using the experimental data of micro-pilot RealCat (a screening platform broadband catalytic activities based in UCCS - Lille) by comparing the modelled and the experimental flowrate values using MATL The second part consists in a catalyst characterization that will determine the cause of the deactivation. In addition to the coking effect that was suspected, the bibliographic research showed a possible link between the loss of molybdenum on the surface of the catalyst (mainly composed of Bi and Mo) and its deactivation. Experimental investigation is required in order to identify the cause of deactivation using advanced techniques such as Temperature Programmed Reduction/ Oxidation (TPR/TPO) and X-Ray photoelectron spectrometry (XPS). The data collected during the structural analysis will help complete the kinetic model.

Illustration : Industrial pilot from Adisséo research lab

Main results

The reactor model is based on a previous thesis [3] and describes efficiently the formation of most of the major products and by-products of the process for fresh catalyst. The reaction rate constants of this model were adjusted using data from the industrial pilot (available in Adisseo research lab) in order to cover larger interval for operating conditions such as the gas temperature.

This model will be a base for a more accurate model that considers the catalyst deactivation effect by adding the data collected during the structural analysis.

The experimental results using TPR/TPO technique provided information about the capacity of oxidation of the used catalyst by comparing it with the fresh catalyst. The observations show a more deactivated sample of catalyst at a certain region of the reactor (results are confidential). This result is included in the model by considering a catalyst activity that varies locally.

The kinetic constants of the rate law describing this local deactivation are adjusted by using accelerated test data of deactivated catalyst such as propylene conversion evolution over time and temperature.

The resulting deactivation rate law is added to the industrial reactor model in order to find the operating conditions that can extend the catalyst life.

References :

[[1] M. Lei, F. Lesage, M.A. Latifi, S. Tretjak, “Optimization of acrolein production in a fixed-bed reactor system, International Conference on Process Control, 2013.

[2] L. Bui and A. Bhan, “A kinetic model for propylene oxidation on a mixed metal oxide catalyst,” Appl. Catal. A, Gen., vol. 564, no. July, pp. 1–12, 2018, doi: 10.1016/j.apcata.2018.07.004.

[3] M. Chateau “Développement d’un réacteur intensifié pour la production d’acroléine”, Ph.D. Thesis, Lorraine University, 2018.

2022

Research subject: Study and modeling of an advanced dissolution process in a continuous reactor – Application to *(U, Pu)O_2* mixed oxydes

German Garzon Losik (3rd year)

Eric Schaer, Alastair Magnaldo[a], Sophie Lalleman[b]

Axe PRIMO| CEA Marcoule – DES/ISEC/DMRC/STDC/LRVE[a] DMCR/SPTC/LDCI[b]

Keywords : Modelling, dissolution, nuclear fuel, fractal surface, mixed oxide

General context, scientific issues :

Dissolution processes, present in a great variety of industries, imposes the use of downstream processes equipment, needed to be efficient and performant as possible.
Dissolution of spent nuclear fuel represents the first chemical step in the reprocessing of the nuclear fuel cycle. The presence of plutonium rich zones in the pellet fuel constitutes nowadays a challenge during its treatment, which inflicts the need of a technological leap forward for the plutonium multi-recycling scenario. Modelling emerges as a useful tool allowing the design and development of new dissolution technologies that must include the most relevant features describing the system

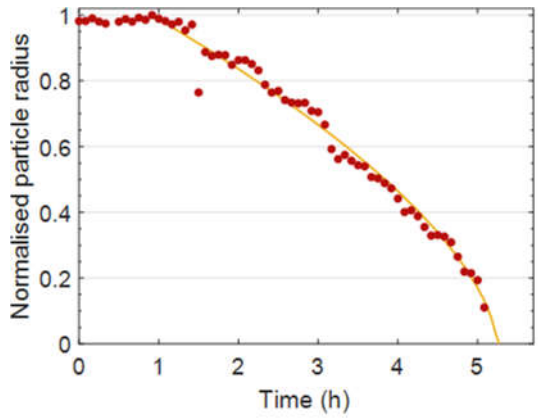
Objectives and stakes :

- Development of a descriptive and predictive model of the different mechanisms that take place during the dissolution of MOX (*(U, Pu)O_2)* powders in nitric acid solution at microscopic scale.
- Design of a new design/process for the dissolution of MOX powder at the macroscopic scale.

Methodology :

This work is divided in two main parts: experimentation and modelling. The experimental part involves the dissolution of MOX powder in nitric acid to determine the intrinsic kinetics of the reaction by using optical microscopy and image processing.
For modeling, a first step is to develop a microscopic model that accounts for the dissolution of a single particle through time. Such approach includes the definition of the reactive surface of the solid through fractal geometry. Indeed, particle surface does not always correspond to something perfectly smooth, but it has some roughness that implies that the dimension can no longer be considered equal to two. Such dimension *D* varies between two to values close to three (highly rough surface). Besides, in some cases the surface where the reaction takes place is not always the same as *D*. This introduces a new parameter in the model (D_R) that can provide information about how and where the reaction actually takes place [1]

Illustration : *UO_2* single particle dissolution in nitric acid through time. (●) Experimental data (—) Model .



Main results

The main equation that describes a single particle dissolution corresponds to:

$$\frac{dr}{dt} = -\alpha v_{disso} r^{D_R - D}$$

Where r is the particle radius, α is a unit conversion constant and v_{disso} is the dissolution rate.
Illustration shows a very good fit of the model to the experimental data for a D_R smaller than D. This means that not all the surface is available for reaction. In other words, the surface characterized by D_R corresponds to the collection of all sites that dissolve. Which either can be the total geometric surface ($D_R = D$) or a subset of specific sites ($D_R < D$) [2].
The latter phenomenon can be explained by the fact that some molecules can be sterically hindered or that parts of the surface are not available for dissolution [1].
Thus, the reaction dimension parameter gives a quantitative idea of surface sensitivity during particle dissolution and improves the understanding about reaction mechanism

References :

[1] Farin, D. and Avnir, D. Reactive fractal surfaces. Journal of Physical Chemistry. 1987 (91) 5517-5521.
[2] Farin, D. and Avnir, D. Use of fractal geometry to determine effects of surface morphology on drug dissolution. Journal of Pharmaceutical Sciences. 1992 (81) 54-57

2022

Design and Preparation of Bio-based Itaconate Elastomer Composites with a Broad Damping Temperature Range and High Performances

Fulan Hao (1st year)

Laurent Falk, Liqun Zhang

Axe PRIMO

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

General context, scientific issues :

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 numerous methods of vibration and noise reduction, One of the solutions is to use polymer materials with excellent damping performances which can absorb vibrational energy and dissipate it as heat energy. [1-3] However, there has been little research on environment-friendly polymer damping materials. Recently, bio-based itaconate elastomers were synthesized by an environmentally benign emulsion polymerization process of bio-based dibutyl itaconate with butadiene, which bore crosslinkable double bonds and many lateral ester groups attached to the polymer backbone. And this new type of bio--based polymer exhibited good physical and damping properties. [4,5] However, it usually only had effective damping performance below the room temperature with a narrow temperature range of 20–30°C, which does not meet requirements for certain applications. Therefore, it is important to prepare bio-based elastomer materials with a high loss factor at room temperature and a broad damping temperature range.

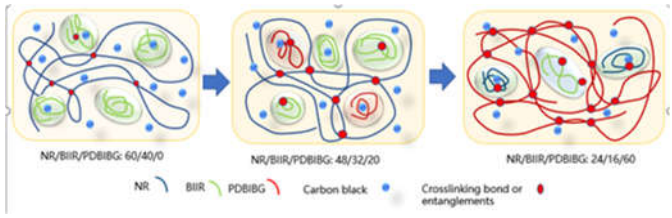
Objectives and stakes :

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

Methodology :

(1) Blending natural rubber (NR), bromobutyl rubber (BIIR) and poly (dibutyl itaconate/butadiene/Glycidyl methacrylate) (PDBIBG) by the mixer to obtain high damping elastomers over a broad temperature range.
(2) Studying the contributions of the crosslink network and the dispersion of fillers in different phases to damping properties.

Illustration : Figure 1 shows the scheme of the structural evolution of the NR/BIIR/PDBIBG blends in the presence of carbon black during blending. With the incorporation of PDBIBG, the continuous phase of NR turned into PDBIBG, and the intermolecular force increased significantly .



Main results

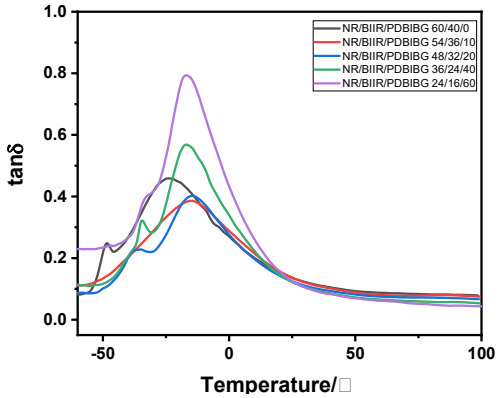


Figure 2. Improvement in damping performances of the NR/BIIR blend by adding PDBIBG

The incorporation of a significant amount of PDBIBG (over 40 parts) in the NR/BIIR blend improves the damping performances of the latter (the wet slip resistance is increased, the rolling resistance is decreased, the loss factor Tan δ is increased, and the damping temperature range is broadened. When the PDBIBG content is 60 parts, the damping temperature range spans over 44°C, which is very significant. This material seems to be an excellent damping material.

References :

[1] Y. Pan, et al. Polym.-Plast. 59 (4) (2019) 385–397.
[2] J. Zhu et al. Polymer 155 (2018) 152–167.
[3] L. Zhu et al. Polym. Test., 93 (2021), 106885.
[4] XX. Zhou et al. Polym. Chem., 2019, 10, 6131–6144.
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2022

Research subject: Microfluidics And Modeling: Two Tools For Determining Kinetic Constants of Mass Transfer In Liquid-Liquid Extraction

Hamza Karim (2nd year)

Christophe Castel, Anne Lelias

Axe PRIMO | CEA Marcoule

Keywords : microfluidics, modelling, mass transfer, liquid-liquid extraction, kinetic rate constants, uranium

General context, scientific issues :

Reactive liquid-liquid extraction is a common operation for the purification of effluents and the recovery of species of interest. For instance, in the nuclear field, the PUREX process is employed, where uranium and plutonium are recovered from spent fuel using TBP as an organic solvent. However, despite the high selectivity towards uranium and plutonium, TBP holds several drawbacks that complicate the recovery process [1, 2]. Hence, new extractants are investigated to replace TBP in the extraction process. Studies conducted by the CEA have shown that monoamides have a great potential in this regard [3, 4]. However, knowledge of extraction kinetics is crucial to judge the performance of these new extractants and to determine whether or not the extraction process can be industrialized.

Objectives and stakes :

Many methods exist to study the kinetics of reactive mass transfer in liquid-liquid extraction. However, recently, there has been an increased interest in microfluidic devices due to their inherent advantages. Thus, this work aims to determine kinetic rate constants of uranium extraction by several extractants using an approach coupling microfluidic devices and mass transfer modeling.

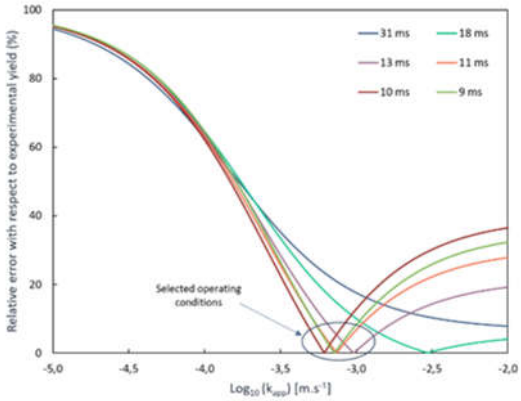
Methodology :

Extraction kinetics of uranium (VI) (10-120 $g.L^{-1}$) from aqueous nitric acid solutions (0.1-5 M) by TBP (5-30 % (v/v)) [5] were investigated using a stratified flow Y-Y shaped microfluidic device. Short residence times were applied to minimize the diffusional contributions and reach the chemical kinetic constant.

Data were modeled using an approach taking into account convection in the axial direction, molecular diffusion in the transverse direction, and a reversible first order reaction taking place at the interface.

Then, the developed model was used to find the appropriate operating conditions for determining the apparent rate constant as shown in the illustration.

Illustration : Determination of appropriate operating conditions ($[U(VI)]_0$ = 10 $g.L^{-1}$, $[HNO_3]$ = 3 M, %TBP = 30 % (v/v))



Main results

Modeling results suggest that the mass transfer was under a mixed regime under the selected operating conditions. The forward apparent rate constant is calculated to be (7,3±2) $x10^{-4}$ $m.s^{-1}$. The latter is much higher than what is predicted by conventional extraction techniques [6], demonstrating the performance of mass transfer in microfluidic devices. Reaction orders with respect to nitrate and TBP were also determined and the intrinsic value of the rate constant was then estimated. Furthermore, the reverse rate constant decreased with increasing nitrate and TBP concentration, suggesting the presence of a more complex reaction mechanism. The next step in the research is to apply the developed model and methodology to investigate the kinetics of monoamide extractants.

References :

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2. Lecomte, M. and B. Bonin, *Treatment and recycling of spent nuclear fuel*. 2008.
3. Cordier, P., C. Cuillerdier, and C. Musikas, *Procédé pour séparer les actinides des lanthanides par extraction sélective des actinides dans un solvant organique comprenant un propanediamide.* Brevet FR, 1991.
4. Miguirditchian, M.a.P.B., *Séparation groupée des actinides à partir d'une phase aqueuse fortement acide, utilisant un extractant solvatant en milieu relargant.* Brevet FR, 2008.

2022

Research subject: Inorganic Materials for Membrane Separations: Molecular Mechanisms and Processes

Margarita Kuznetsova (2nd year)

Christophe Castel, Laëtitia Cesari

Axe PRIMO

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

General context, scientific issues :

Membrane-based processes are widely used in industry for separation and purification of different gas mixtures like CO_2/CH_4, CO_2/N_2, N_2/O_2 and many others. Inorganic zeolite membranes have been extensively studied for these applications as they are beneficial in terms of thermal and chemical stability, high permeability and selectivity as well as the possibility to integrate reaction and separation in a single unit [1]. The zeolites have pores of molecular size which make them promising molecular sieves. However, mass transport mechanisms in the porous membranes are complex and their quantification is challenging. The studying of zeolite membrane application for the gas separation has already started at LRGP laboratory [2].

Objectives and stakes :

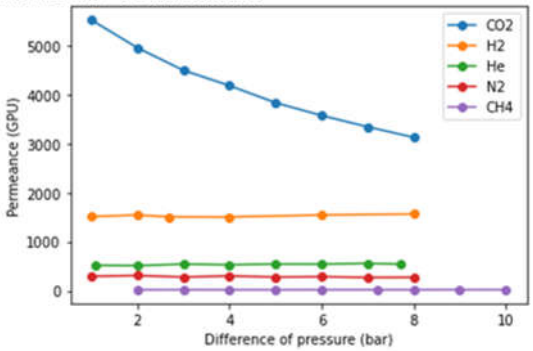
This work aims to evaluate the efficiency of the zeolite porous membranes for the gas separations through a multi-scale study coupling macroscopic and microscopic levels. The transport mechanisms as well as coupling phenomena are going to be investigated

Methodology :

Methodology of this PhD thesis involves:- Experimental measurements of the membrane performance using different zeolite membranes (chabazite, MFI). Pure gas permeance values are determined at different operating conditions (T, P) and membrane selectivities are evaluated. Future tests imply studying of gaseous mixtures.

- Molecular simulations using Grand Canonical Monte Carlo (GCMC) technique enabling one to determine adsorption isotherms, Equilibrium Molecular Dynamics (EMD) calculations of diffusion coefficients (self-diffusion, Maxwell-Stefan and Fick) and Non-Equilibrium Molecular Dynamics (NEMD) experiments allowing the direct determination of the permeance. These numerical data are going to be compared with experiments.- Modelling of the transport phenomena in porous media in order to represent involved mechanisms and to calculate mass transport parameters.

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



Main results

The results of laboratory experiments provided with a high-performance chabazite membrane show that permeance of different pure gases in porous media depends on several parameters such as: (i) preferential adsorption of CO_2 as its permeance is not stable and decreases with Δp; (ii) molecular sieves effects - molecules having bigger kinetic diameter have lower permeance, like CH_4 which diameter is similar to the pore openings (3.8 Å).

Molecular simulations are performed in order to have a deep insight into the molecular scale interactions. Firstly, experimental adsorption isotherms from literature are reproduced with GCMC method proving a right choice of force fields. Secondly, different intra-crystalline diffusion coefficients are determined with EMD and compared with literature data. Future work is to model the permeance with 1D equations as a combination of diffusion and/or adsorption contributions and to obtain the permeance directly via NEMD simulations. The data are to be compared either with experiments or with literature.

References :

[1] P. F. Zito, A. Caravella, A. Brunetti, E. Drioli, et G. Barbieri, « Knudsen and surface diffusion competing for gas permeation inside silicalite membranes », *J. Membr. Sci.*, vol. 523, p. 456-469, févr. 2017, doi: 10.1016/j.memsci.2016.10.016.

[2] S. Picaud Vannereux, Étude expérimentale et simulation de procédés hybrides intégrant des membranes zéolites et polymères pour la purification d'hydrocarbures gazeux biosourcés par perméation de vapeurs, thesis, Université de Lorraine, 2019

2022

Research subject: Transmembrane distillation for recovery of industrial aqueous effluent

Andres Martinez (3rd year)

Christophe Castel, Thibaut Neveux

Axe PRIMO | EDF

Keywords : Membrane distillation, Industrial effluents, process system engineering.

General context, scientific issues :

Chemical products used in industrial processes generate liquid and gas effluent to be treated. Thermal power plants generate wastewater mainly from withdrawal of the water circuits containing key chemical substances. Nowadays, those effluents are treated with high energy demanding technologies e.g evaporation, to accomplish the actual environmental regulation.

Membrane technologies are a potential alternative to improve energy and productivity performance. Reverse osmosis is already deployed for desalination at industrial scale, but it has technical limitations while treating high-salinity brines [1].

Membrane distillation is intensively investigated as an alternative or complement to achieve high-salinity wastewater treatment, however, there are still some technical challenges [2].

Objectives and stakes :

This research study aims to provide alternatives process to the wastewater treatments for those used in today's plants. It will propose a generalized solution to achieve better energy performance. It also targets the evaluation of a key chemical recycling.

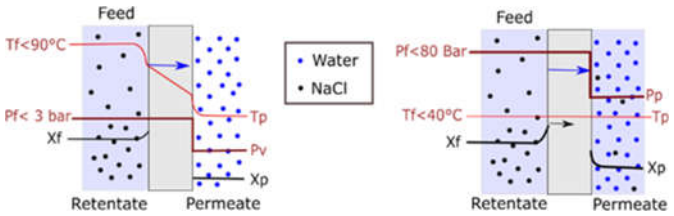
This work will provide a hybrid technology process evaluation for a selective recovery of chemical substances from industrial effluents.

Methodology :

iComputer-aided process simulation is the main tool deployed to do a systematic comparison of process performance. This tool is based on a superstructure optimization [3] of membrane modules coded into a dedicated in-house unit and performed in ProSimPlus. However, the toolbox code requires parameters to calculate mass and heat transfer adapted to wastewater composition e.g permeance of each component through the membrane and thermodynamical properties for aqueous mixtures. That information is available for a sodium chloride / Water solution but not for all the other components present in power plants liquid effluents.

Then, an experimental installation is deployed to calculate permeances through membrane modules of two binary systems of interest.

Illustration : General schema of transfer phenomena through a membrane for:



a) Distillation Transmembranaire b) Reverse osmosis

Main results

A generic map of key performance indicators for MD, RO and MSF is obtained as the main result, with the associated optimal process design (number of stages) and operating conditions (pressure, temperature, stage cut).

- The experimental installation is deployed to measure permeance of different membranes for membrane distillation on sweep gas operation mode (SGMD). The methodology to obtain mass transfer parameters is set up and tested with three different hollow fiber modules.
- Mass transfer measures were conducted for two systems: water with a component A and B, where A is more volatile than water (e.g Ammoniac) and B is less volatile than water.
- Experimental data were treated with the dedicated code for permeance calculation under experimental conditions.

Perspectives

Results of experimental methodology will provide data to support the toolbox for superstructure optimization. Those results will lead to a better prediction to guide process synthesis on liquid effluent treatments for power plants. .

References :

[1] EDF, « Centrales nucléaires et environnement – prélèvement d'eau et rejets », 2015 – 258 p. , 2018

[2] D. Mejia Mendez, C. Castel, C. Lemaitre and E. Favre, «Membrane distillation (MD) processes for water desalination applications. Can dense selfstanding membranes compete with microporous hydrophobic materials? », Chemical Engineering Science, 188, p 84–96, 2018

[3]Q. Zhao, T. Neveux, M. Mecheri, R. Privat, P. Guittard, J. Jaubert. Superstructure optimization (MINLP) within ProSimPlus Simulator. Computer Aided Chemical Engineering, 2018. 767–772.

2022

Research subject: Modeling and optimization of low pressure carburizing furnaces

Fatima Matamoros Marin (4th year)

Abderrazak M. Latifi, Pierre-Alexandre Glaude, Roda Bounaceur, Hubert Monnier

Axe PRIMO

Keywords : Carburizing furnace, Pyrolysis, Modeling, Simulation, Optimization

General context, scientific issues :

Low pressure carburizing (LPC) is a thermochemical process that aims to strengthen the surface of metals by increasing the carbon concentration at their surface. These metals are then used by the automotive or aerospace industry. A major drawback of LPC is that it produces toxic compounds (mainly Polycyclic Aromatic Hydrocarbons (PAH) and soot) to which workers are exposed during the maintenance of carburizing furnaces

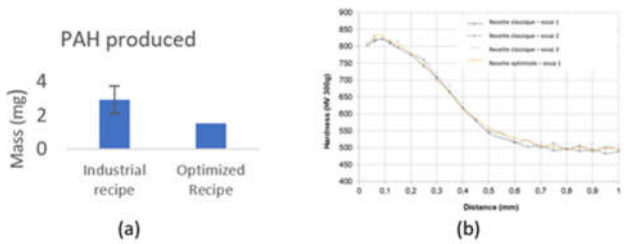
Objectives and stakes :

This thesis deals with the development of an optimization methodology for low-pressure gas carburizing furnaces. The objective is to determine safer operating conditions for workers exposed to the toxic by-products that are generated, i.e. PAH and soot while guaranteeing the carbon content and hardness of the metal.

Methodology :

A first principle model of the process involving the three stages of carburizing, i.e. pyrolysis of acetylene [1], a heterogeneous surface reaction that produces solid carbon and the diffusion of the latter into the bulk of a metal was established. Experiments conducted on a laboratory scale tubular reactor and a jet stirred reactor were then carried out, as well as experiments on an industrial low-pressure gas carburizing furnace by adopting an industrial "recipe", i.e. predetermined operating conditions established by trial and error basis in order to meet the desired carburizing depth. The experimental results were exploited to validate the model. The model was used in the formulation of the dynamic optimization problem which aims to minimize the production of toxic compounds while ensuring the industrial quality of the carburized steel parts. Equality and inequality constraints were added on the state variables to ensure the quality of the treated steel parts. The resulting problem is a mixed integer dynamic optimization problem of infinite dimension.

Illustration : PAH (a) and hardness of the treated steel parts (b) obtained with the industrial and the optimized recipe



Main results

The optimization problem of infinite dimension was transformed into a finite-dimension problem by means of the control vector parameterization approach and the optimization algorithm was implemented within the MATLAB environment. The ordinary differential equations of the model are integrated using the MATLAB ode suite and the SQP algorithm of solver fmincon is used to solve the optimization problem. The outputs of the optimization, i.e. the decision variables, are the operating conditions of the process: the number of cycles (determined by the method proposed by Chachuat et al. [2]), the lengths of boost and diffusion stages and the inlet volumetric flowrate of acetylene.

Experiments using the new operating conditions were conducted in the industrial furnace. The results corroborate that the optimized recipe leads to less PAH production (Illustration (a)) and steel parts of the same quality as the industrial recipe, i.e. same hardness (Illustration (b)).

References :

[1] T. Bensabath, 2017, Approche préventive pour une réduction des Hydrocarbures Aromatiques Polycycliques (HAP) dans les fours à pyrolyse, PhD thesis, Université de Loraine, France.

[2] B. Chachuat, N. Roche, and M. A. Latifi, “Optimal aeration control of industrial alternating activated sludge plants,” Biochemical Engineering Journal, vol. 23, no. 3, pp. 277–289, 2005

2022

Research subject: Membrane Process for Helium Purification (PROMET-Hé)

Amina Najib (Research Engineer)

Christophe Castel, Eric Favre, Egle Ferreri, Anaelle Cloteaux, Claire Ethgen

Axe PRIMO | 45-8 Energy

Keywords : Membrane Separation Process, Helium, Permeance, Selectivity, Process Synthesis, Simulation

General context, scientific issues :

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

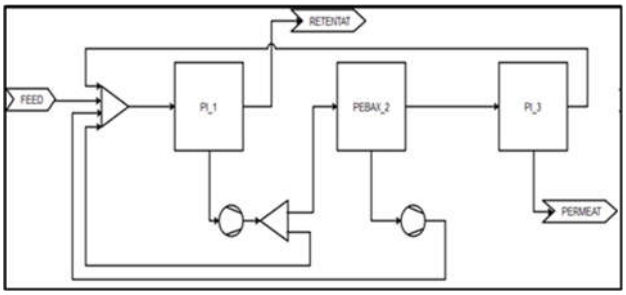
Objectives and stakes :

The main objective of Promet-Hé is to produce helium gas with a much lower energy consumption than the traditional process based on separation gases by liquefaction, extremely costly and energy-intensive in the case of helium, liquefying at -269°C. A recovery of 95% of helium is targeted with a purity, which can be adjusted according to customer needs, from 95% to 99.999%. The valorization of co-products will also increase the profitability of the project. An innovative, mobile and compact separation process based on membrane technology will be developed that will have to adapt to the specificities of new geological contexts (shallow depths) and be applicable on an

Methodology :

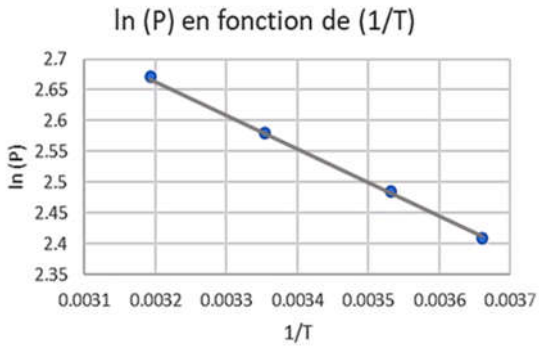
To obtain a good separation performance, it is necessary to choose judiciously the membrane materials, the architecture of the process and the operating conditions. The gas extracted from the subsoil mainly consists of He, CO2 and N2. Experimental tests were carried out at the LRGP to measure the permeance for several commercial modules based on different membrane materials. Using those experimental permeance data, a process synthesis methodology has been carried out to optimize the architecture of a membrane separation process through a cost objective function, allowing multi-stage and multi-membrane architectures. MEMSIC, a software developed at LRGP for simulating multi-constituent separation through a gas permeation membrane module, is then used to simulate the membrane separation process depending on the operating conditions. [2] The objective of this pre-study is to study the main principles of conception and design of the process (size and type of modules, pressures, unit operation, etc.) and assess their industrial robustness through sensitivity analysis. These outlines will be discussed later on with the equipment manufacturer in charge of the pilot construction

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



Main results

For He/N2 separation, it is possible to have access to materials with high selectivities and exhibiting good permeabilities. It's the case including polyimides, some of which are commercially available (e.g.: Evonik, UBE…). Meanwhile, He/CO2 system, has a particularity: it is possible to have access to materials selective to He (selectivity He/CO2 >1) or selective to CO2 (He/CO2 selectivity < 1) but the performance of commercial materials is quite low with few materials with selectivities greater than 10 or less than 0.1. By elsewhere, some non-commercial materials show interesting selectivities. The experimental obtained results, and particularly the temperature dependence of the permeances, were compared with those reported in the literature. The first results using process optimisation clearly show the interest of a multi-stage architecture using different types of membranes. The targeted helium purity and recovery rate constraints are accessible



References :

[1] M. Lord, "Elements in focus : helium," no. 53, pp. 1–5, 2021.

[2] R. Bounaceur, E. Berger, M. Pfister, A. A. Ramirez Santos, and E. Favre, "Rigorous variable permeability modelling and process simulation for the design of polymeric membrane gas separation units: MEMSIC simulation tool," *J. Memb. Sci.*, vol. 523, pp. 77–91, 2017,

2022

Research subject: Process design by superstructure optimization for Combined Cooling, Heating and Power (CCHP) systems.

Andrés Piña-Martinez (ATER)

Jean-François Portha

Axe PRIMO

Keywords : : Process synthesis, Superstructures optimization; Combined Cooling, Heating and Power (CCHP) cycles, Multi-criteria optimization, MINLP.

General context, scientific issues :

One of the strategies to achieve the target of 32% share of EU energy consumption coming from renewable energy sources (RES) by 2030 is to increase the use of distributed energy systems (DES). The promotion of DES has opened the way to different technologies such as combined heat and power (CHP) or combined cooling, heating and power (CCHP) systems. Recently, a novel CCHP cycle, operating with two-phase expanders and compressors, has been designed. Such a cycle enables the development of an all-in-one device capable of producing electric, heating and cooling power with a single working fluid. Among the design challenges of this novel CCHP/CHP system, the working-fluid [1] and architecture selection appears as key stages of its development.

Objectives and stakes :

In terms of architecture, a CHP cycle may include different variations such as: regeneration, reheating, superheating or bleeding. The current research work aims: 1) to study how the above variants can be adapted to a CHP application; 2) to automatically design the optimal architecture of the CHP process. For the process design problem, a superstructure optimization approach has been implemented [2].

Methodology :

To consider the flowsheet configuration as a degree of freedom during optimization, it is decided to define a superstructure of the CHP process including all possible flowsheet sub-configurations. The selection of a path among the superstructure can be controlled by a switch unit whose position depends on a binary variable (see Illustration).

The superstructure, which contains 60 sub-structures, has been implemented in the CAPD software ProSimPlus® following the methodology proposed by Quintero- Masselski et al. [3]. In order to assess the pertinence of the studied process structures, two objective functions are defined for the superstructure optimization:

1. Energy utilization factor.
2. Levelized cost of electricity production.

Illustration : Switch for path selection

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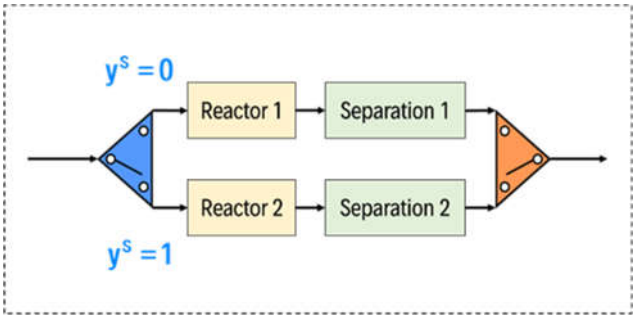
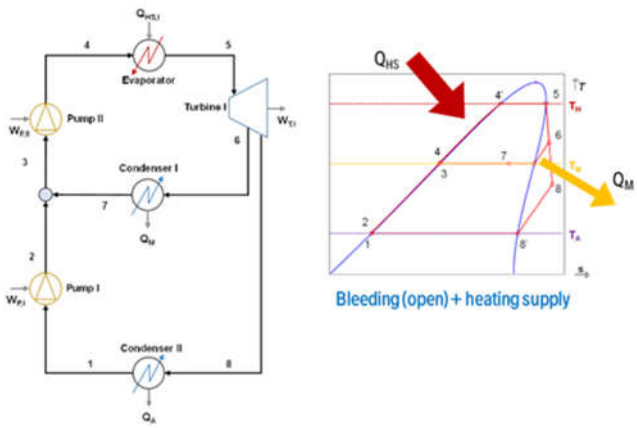


Main results

Preliminary results include 2 optimal points from a total number of solutions reaching 7 000, among which 50% of them are feasible (full respect of constraints). Such results suggest that the optimal CHP process should contain two turbine bleedings, one for the end-user heat supply (see figure below), and another one for heat integration.



References :

(1) Pina-Martinez, A.; Lasala, S.; Privat, R.; Falk, V.; Jaubert, J.-N. Design of Promising Working Fluids for Emergent Combined Cooling, Heating, and Power (CCHP) Systems. ACS Sustain. Chem. Eng. 2021, 9 (35), 11807–11824.

(2) Mencarelli, L.; Chen, Q.; Pagot, A.; Grossmann, I. E. A Review on Superstructure Optimization Approaches in Process System Engineering. Comput. Chem. Eng. 2020, 136, 106808.

(3) Quintero-Masselski, C.; Portha, J.-F.; Falk, L. Conception and Optimization of an Ammonia Synthesis Superstructure for Energy Storage. Chem. Eng. Res. Des. 2022, 177, 826–842. https://doi.org/10.1016/j.cherd.2021.11.039.

2022

Research subject: Superstructure optimization approach for process design for the industry of the future (PROFUTUR)

Christian Steven Quintero Masselki (4th year)

Laurent Falk, Jean-François Portha

Axe PRIMO

Keywords : Process design, superstructure, ammonia synthesis, MINLP optimization, energy storage

General context, scientific issues :

Storage of energy is a trending reality and favours the integration of renewable energy in the energy market. This work is oriented on conceiving an optimal process for ammonia synthesis for the chemical storage of renewable energy, using a methodology based on superstructure optimization. A superstructure can be defined as the representation including several alternatives to perform a process, which are simultaneously evaluated to determine the best process configuration. Its resolution requires an optimization algorithm to handle MINLP problems.

Illustration :

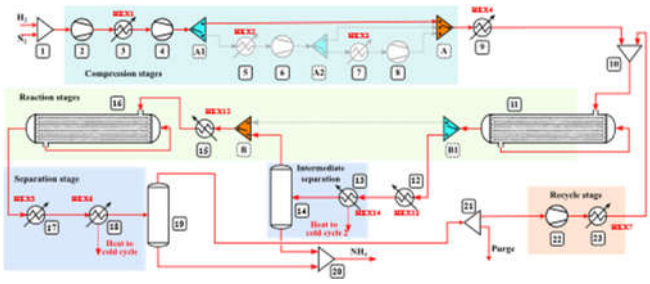


Fig. 2. Superstructure representation of the optimal solution (red)

Objectives and stakes :

The main objective is to determine the set of optimal configurations allowing to minimize the Levelized Cost of Ammonia (LCOA), while maximizing the energy efficiency of the process. Among the structural alternatives, there exists the choice of: the reactor configuration (multibed adiabatic and multitube autothermal) and the number of reactors, the catalyst, the separation technology (condenser, membranes, PSA), the use of intermediate separation and the type of cooling (indirect or direct).

Methodology :

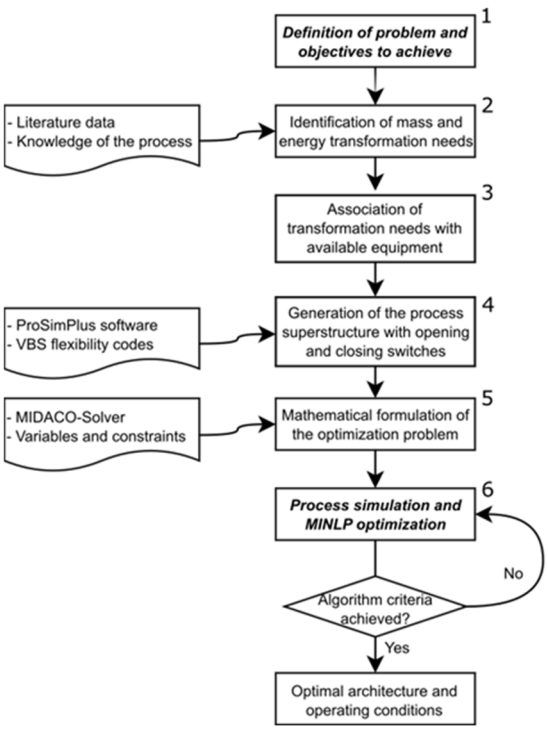


Fig. 1. Methodology for the superstructure optimization

Main results

Four superstructures were optimized to determine the best reactor configuration and the most suitable separation technology. The best solution was obtained for the use of Ru-based catalyst, two autothermal reactors in series, with intermediate and final separation by condensation, while using 2 compressors in the compression stage. The synthesis pressure for this solution is 100 bar, allowing to reduce in 33 % the pressure regarding the conventional Fe-based catalyst.

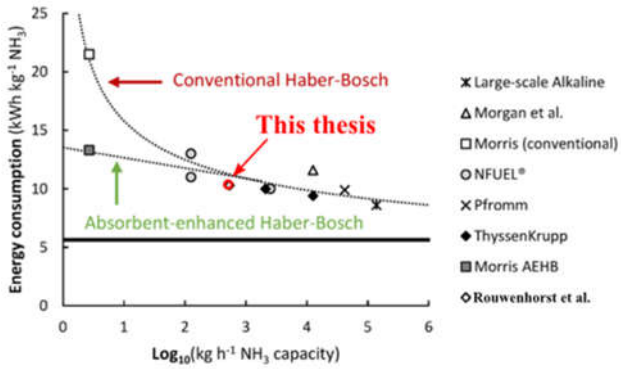


Fig. 3. Results of the energy consumption and the ammonia production regarding data from literature [1].

This configuration reaches an LCOA of 790.3 €/t, competitive regarding the ammonia production with natural gas (1500 €/t in April 2022 in Europe) and an energy efficiency of 67.1 %, almost ten point higher than the adiabatic configuration. The scenario represents a power consumption of 5.10 MW to store 2.58 MW in ammonia, for a total power consumption of 10.23 kWh/kg.

References :

[1] Rouwenhorst KHR, Van der Ham AGJ, Mul G, Kersten SRA. Islanded ammonia power systems: Technology review & conceptual process design. Renew Sustain Energy Rev 2019;114

2022

Research subject: Dynamic modelling under uncertainty for incinerator supervision

Lionel Sergent (1st year)

François Lesage, Abderrazak Latifi

Axe PRIMO | SUEZ

Keywords : Dynamic modelling - Uncertainty - Supervision – Incineration - Waste Treatment - Process Control

General context, scientific issues :

Incineration is a widely used waste treatment technique. Its sanitizing and volume reduction abilities, alongside the recovered energy explains its prevalence in many countries for the treatment of both household and industrial waste. Despite advances in equipment, fine and stable control of the process remains difficult, mostly because of the heterogeneity of the waste fuel and the lack of local measurements. Troubleshooting in incineration plants is also often impaired by the lack of scientific understanding. A model adapted to these difficulties is expected to bring significant opportunities for operational improvement.

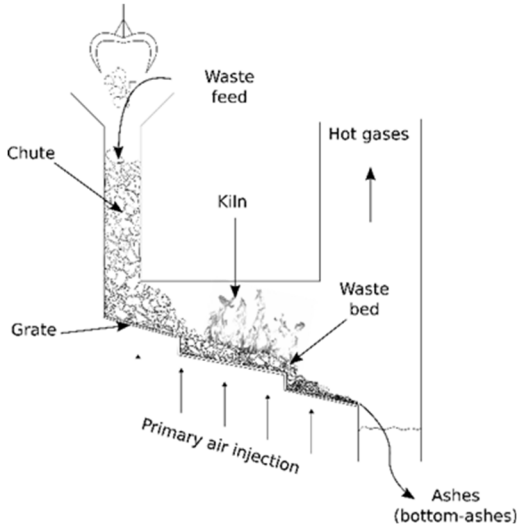
Objectives and stakes :

The main objective is to produce a model able to predict the behavior of the key operating variables. Compared to other works of the same kind, the model must be able to be calculated in real-time. The unavoidable uncertainties are to be coped with. The scope is the whole main process: from the waste feed to the stack. The kiln is the most critical and complex unit in the process and modelling the combustion in a way that is suitable for real-time calculations is one of the main challenges.

Methodology :

The model being built is separated into units whose delimitations are conventional in the industry. The sub-models are based on conservation principles. The phenomena are modelled using semi-empirical laws found in the literature. The corpus on waste incineration is small [1][2][3], so literature on biomass combustion [4] and other processes is also screened. Depending on the unit, the representation used is either 0D, 1D or 2D. For non-0D, the partial differential equations obtained are discretized using the finite volumes method. The resolution is done using a MATLAB code specifically developed. Once the model brings satisfaction, it is expected to develop a state observer. The predictions are to be compared with measurements of a SUEZ operated household waste incinerator in Alsace. Once the model brings satisfaction, its applicability to online use is to be explored.

Illustration : Overview of a grate waste incinerator



Main results

No original results were obtained yet.

The literature for waste characterization and combustion was thoroughly reviewed, while the literature around biomass combustion and other related industries was sparsely reviewed.

The reproduction of some models found in the literature has been undertaken to verify the same results could be obtained. Some results were successfully reproduced while others are still under development. Such a reproduction will also allow a preliminary sensitivity analysis to guide the choices to be made for the final model.

References :

[1] Menard, Y. Modélisation de l'incinération sur grille d'ordures ménagères et approche thermodynamique du comportement des métaux lourds. 2003, PhD thesis.

[2] Yang, Y. ; Goh, Y. ; Zakaria, R. ; Nasserzadeh, V. ; Swithenbank, J. Mathematical Modelling of MSW Incineration on a Travelling Bed. Waste Management 2002, 22, 369-380

[3] Van Kessel, R. Stochastic Disturbances and Dynamics of Thermal Processes. 2003 PhD thesis.

2022

Research subject: Multi-physical modeling of the corrosion-erosion process: case of a liquid jet containing particles

Vinícius Soares Teixeira (defended on 11th of may 2022)

Benoit Gwinner, Tojonirina Randriamantena, Sophie Charton, Eric Schaer

Axe PRIMO | SCCME, CEA

Keywords : : corrosion-erosion, abrasive particles, erosion rate, zirconium

General context, scientific issues :

Corrosion-erosion of a ductile and subject material is the result of a combination of different degradation phenomena (chemical and electrochemical, mechanical) which make it difficult to understand. In order to estimate the contribution of each phenomenon, different approaches have already been proposed in the literature [1-2]. It is well recognized that, in addition to the contribution of "only" corrosion and erosion, there is a contribution of a synergistic term between these two phenomena which contributes to the loss of material observed experimentally

Objectives and stakes :

In the 1st year, we were particularly interested in the corrosion behavior of Zr and in the determination of its repassivation kinetics. The various tests carried out made it possible to establish a panel of knowledge on the "only" corrosion behavior and the influence of erosion on the corrosion of Zr in HNO_3 4 mol L^{-1} medium at room temperature.

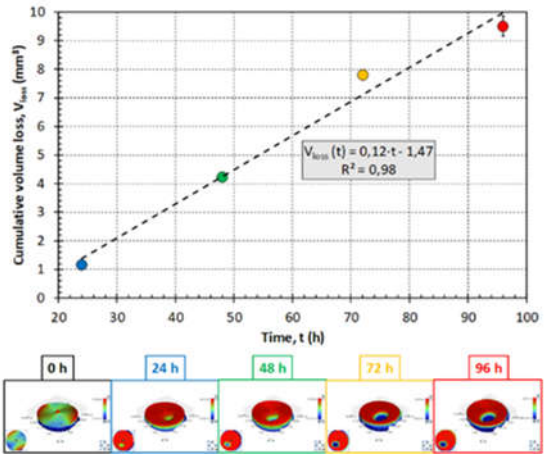
During the 2nd year, the objective is to study the performance of Zr when it is subjected to the action of a jet enriched (or not) with abrasive particles and to determine the contribution of the "only" erosion and the possible influence of corrosion on erosion. We want to know the influence of the variation of the different experimental parameters on the loss of mass of Zr over time.

As an illustration, the results obtained in water under the experimental conditions presented in the next section will be presented.

Methodology :

The test (carried out in a submerged jet device) decomposed into 4 periods of 24 h, with the renewal of the solution (water + abrasive particles in 316L steel) between each period, in order to study the behavior of the material over time. After each period, analyzes with an interferometric confocal microscope (determination of the depth of the crater formed after the impacts) and gravimetric measurements (estimation of the loss of mass of the sample) were carried out.

Illustration : Above, evolution of the volume loss kinetics (mm^3) as a function of time (h) of a Zr sample subjected to an erosion test in water with abrasive particles (jet speed: 4.3 m s^{-1}, abrasive concentration: 22.4 kg m^{-3} and mean diameter of the powders: $3.5 \cdot 10^{-4}$ m). Below, images of the crater formed on the sample after the different periods.



Main results

The result presented in the Figure shows that the cumulative mass loss increases during the different periods. This indicates that the crater formed in the sample – by the action of the fluid loaded with particles – becomes deeper with the test time (as observed in the images obtained by interferometric microscopy at the bottom of the Figure). The kinetics of loss of volume have a cumulative and linear character, which results from the degradation of material entrained by the abrasive jet. By transposing the loss of volume into loss of thickness, it is possible to determine an approximate erosion rate (mm $year^{-1}$). Under these conditions, it is of the order of 8.5 mm $year^{-1}$. For comparison, in HNO_3 without abrasive particles, the corrosion rate of Zr is less than 10 µm $year^{-1}$. This shows the effect that the presence of abrasives can have on its behavior in a given medium

References :

[1] M. M. Stack, N. Pungwiwat, *Wear*, v. 256, n. 5, 565-576, 2004.

[2] ____, G. H. Abdulrahman, *Tribology International*, v. 43, n.7, 1268-1277, 2010.

2022

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

Di Wu (3rd year)

Jean-Marc Commenge, Laurent Falk

Axe PRIMO | AUER

Keywords : Microcogeneration, Steam Methane Reforming, HT-PEMFC, heat-exchanger reactor, fuel partialization, exchange network.

General context, scientific issues :

Global warming is a severe environmental issue that has drawn the attention of the scientific community to propose reduction strategies of carbon dioxide emissions related to their numerous sources. Among these sources, buildings account for about 40% and 36% of the total European energy consumption and greenhouse gas (GHG) emissions respectively [1]. Around 75% of the total European building floor area correspond to residential buildings [2], where the vast majority (up to 80%) of energy use and emissions are related to heating applications [3]. Since the 1990s, micro-cogeneration or micro-CHP has been proposed as a possible alternative to gas-fired boilers for households. In terms of efficiency, for the same amount of production of electricity and heat, CHP systems require 30% less primary energy compared to central production plants. This gain in energy efficiency immediately translates into economic and environmental gains through a 30% reduction in associated greenhouse gas emissions.

Objectives and stakes :

The aim of the present work is to combine process simulation and experiments to analyze the feasibility and interest of micro-cogenerator as a solution of energy transition applied to novel individual buildings, focusing here on a HT-PEMFC-based 1 kWel micro-CHP system including a microstructured heat-exchanger-reactor for intensification of the steam reforming step.

The model of heat-exchanger-reactor and HT-PEMFC is developed separately from the entire process of HT-PEMFC based micro-CHP system. The integration of these unit models in a complete process with all other components of the plant should be performed and validated.

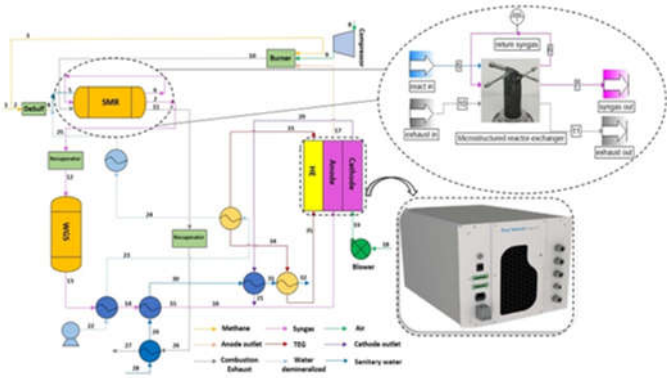
Moreover, to ensure the feasibility of µ-CHP system. A multi-objectives process optimization should be carried out based on the results from process parametric study by considering not only the system performance index but also the different operating modes.

Methodology :

The experimental campaign consists of the test bench integrated, used to carry out the experimental campaigns and identify the influence of operating parameters. The simulation model of the process and its sensitivity analysis are performed in ProSimPlus®, a process simulation software. The system optimization is performed with the external optimizer MIDACO Solver, an evolutionary algorithm for MINLP resolution.

The electrical and thermal efficiencies are chosen as objective functions for system full-load and partialization operating modes with 5 decision variables and 7 inequality constraints

Illustration : Schematic view of the HT-PEMFC based plant.



Main results

Due to a numerical restriction in the exchanger-reactor simulation module, the multi-objective optimization is carried out in multi-run mode using different initializations and changing the optimization parameter (i.e. seed) in order to exploit a more integrated form of Pareto front. The feasible solutions have been selected for further analysis.

References :

[1] de Groote Maarten RO. The active role of buildings in a transforming energy market. 2015.

[2] Atanasiu B, Maio J. Europe's buildings under the microscope. A country-by-country review of the energy performance of buildings. 2011.

[3] Merkel E, McKenna R, Fehrenbach D, Fichtner W. A model-based assessment of climate and energy targets for the German residential heat system. Journal of Cleaner Production 2017;142:3151–73. https://doi.org/10.1016/J.JCLEPRO.2016.10.153.





BIOPROMO

BIOPROCESS, BIOMOLECULES

LRGP
LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

2022

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

Alejandro Avilan Garzon (1st year)

Eric Olmos, Bruno Ebel, David Pfister

Axe BIOPROMO | Ypso Facto

Keywords : Modelling, Bioprocess, Monoclonal antibody (mAb), Chinese Hamster Ovary cells (CHO)

General context, scientific issues :

Monoclonal antibodies (mAbs) represent nearly 50 % of the therapeutic protein market. More than 70 % of these antibodies are currently produced by the CHO cell lines [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. However, the construction of these twins requires models, ranging from the microscopic (intra-cellular mechanisms) to the mesoscopic (tank hydrodynamics) that would be capable of integrating all the process data necessary for the quantification and prediction of performance indicators (growth rate, productivity, and product quality).

Objectives and stakes :

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

Methodology :

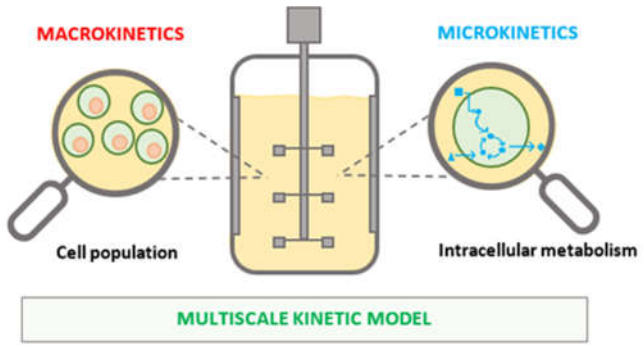
Experimental data: Collection of experimental kinetic data of CHO cell cultures from the literature and complemented by data generated in the laboratory in batch and fed-batch cultures at the Erlenmeyer flasks and stirred tank bioreactor scale.

Microkinetic modelling: Distribution of intracellular fluxes and modelling of the intracellular metabolism to simulate the obtained experimental data.

Macrokinetic modelling: Development of mechanistic and/or statistical macrokinetic models to predict the impact of changes in culture conditions.

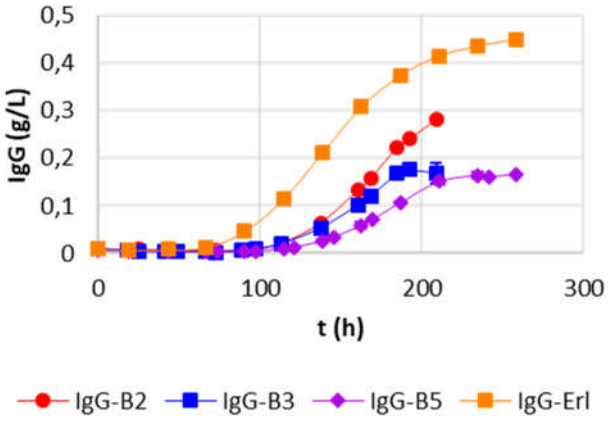
Real-time piloting: Evaluation of the predictive relevance of the models built by estimating and correcting culture trajectory in real time to optimize process control.

Illustration : Multiscale modelling



Main results

Kinetic data of cell cultures of CHO producing monoclonal antibodies were generated at the scale of Erlenmeyer flasks (100 mL) and controlled mini bioreactor (200 mL). More data expected to be generated using different culture conditions to capture different phenomena and to expand the validity range of the developed models.



The basis of a kinetic model using intracellular metabolism was established. It is expected that the results of the microkinetic simulations/internal flux distribution will allow the establishment of an intracellular network that will correctly represent the changes in metabolism evidenced during animal cell culture.

References :

[1] Frenzel, A., Hust, M., & Schirrmann, T. (2013). Expression of recombinant antibodies. In Frontiers in Immunology. 4, 217.

2022

Research subject : Development of addressed nanoparticles for X-ray activated anticancer photodynamic therapy

Batoul Dhaini (3rd Year) Cotutelle Lebanon /France

Céline Frochot (LRGP), Tayssir Hamieh (MCEMA, Lebanon)

Axe BIOPROMO

Keywords : Photodynamic therapy, Nanoparticle, peptide, X-Ray, Reactive Oxygen species, Singlet Oxygen

General context, scientific issues :

The principle is to produce singlet oxygen, after the excitation of nanoparticle (NP) by X-rays. A photosensitizer (PS) is coupled to the nanoparticle as well as a peptide for NRP-1 active tumor targeting (collaboration LCPM UMR 7375) [1,2]. The use of X-rays allows penetration into deep tissues to overcome the limitation of light penetration [3].

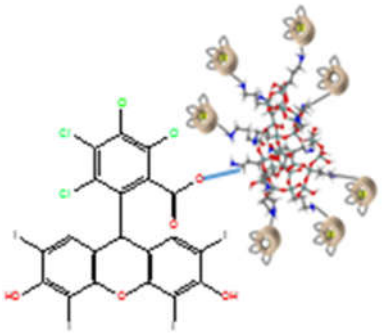
Objectives and stakes :

The nanoparticles used are chelated with lanthanides. After the excitation of these nanoparticles by X-rays, the lanthanides emit luminescence that is absorbed by the photosensitizer. An overlap between absorption spectrum of the PS and the emission spectrum of the lanthanides is required allowing to have an energy transfer between these two species. Following this energy transfer, the PS is activated and produces singlet oxygen in an oxygenated medium.

Methodology :

Before the synthesis of NP@PS, the confirmation of the energy transfer between lanthanides and PS is essential. The variation of luminescence intensity and lifetime as a function of PS concentration was studied.
The NPs used are AGuIX with chelated Gadolinium or Terbium. These NPs are in phase two clinical trials. These NPs are coupled to Rose Bengal (RB) as a PS. This covalent coupling is realised directly on the nanoparticles or through a spacer arm. Two types of spacer arms were evaluated: bromohexanoic acid (ester bond) or aminohexanoic acid (amide bond). This allows to confirm the stability of the amide bonds compared to the ester bonds in the biological medium. For active targeting DKPPR and NKRTR peptides were synthesized as targeting vectors to the NRP-1 receptor overexpressed in several tumor types and neovessels. These peptides were coupled via an amide bond to the RB. After transformation of the amine groups of AGuIX in SH, a maleimide was coupled to the RB-peptide. The maleimide-lysine(RB)-peptide was coupled to the AGuIX by a sulfide bond.

Illustration : AGuIX@RB



Main results

The energy transfer between free Terbium or Gadolinium ions and the RB was confirmed in solution. This FRET type energy transfer was also confirmed between the NPs and the RB before coupling.
After the covalent coupling between the RB and the AGuIX with and without arms, an energy transfer under X-ray was confirmed (collaboration CRAN UMR 7039). Singlet oxygen production was confirmed by using SOSG and DPBF. The energy transfer was more important for NPs coupled to a RB with arm than AGuIX@RB without arm. This might be due to steric hindrance around the AGuIX when coupled directly to the RB.
The size of these AGuIX was between 4 and 7 nm. The zeta potential of AGuIX coupled to the RB was greater in absolute value than AGuIX alone, confirming that these AGuIX were stable in solution.

References :

[1] E. Thomas , L. Colombeau , M. Gries , T. Peterlini , C. Mathieu, N. Thomas et al., “Ultrasmall AGuIX Theranostic Nanoparticles for Vascular-Targeted Interstitial Photodynamic Therapy of Glioblastoma”, International Journal of Nanomedicine, vol. 12, pp. 7075-7088, 2017.

[2] B. Dhaini, B. Kenzhebayeva, A. Ben-Mihoub, M. Gries, S. Acherar, F. Baros, *et al.*, "Peptide-conjugated nanoparticles for targeted photodynamic therapy," *Nanophotonics,* vol. 10, pp. 3089 -3134, 2021.

[3] L. Larue, A. Ben Mihoub, Z. Youssef, L. Colombeau, S. Acherar, J. C. André, et al., "Using X-rays in photodynamic therapy: an overview," Photochem Photobiol Sci, vol. 17, pp. 1612-1650, 2018

2022

Research subject : Screening, Separation and Identification of Metal-Chelating Peptides in Protein Hydrolysates

Jairo Andrés Camano Echavarria (1st year)

Laetitia Canabady-Rochelle, Katalin Selmeczi

Axe BIOPROMO

Keywords : Protein, Enzymatic hydrolysis, Hydrolysate, Screening, Separation, Identification, Biofunctionality, Metal-chelating peptides, Fish processing co-products, Agro-industrial byproducts, Tilapia scale.

General context, scientific issues :

Bioactive Peptides (**BPs**) are biological compounds, naturally encrypted within protein sequence under an inactive form and released upon proteolysis. Nowadays, these peptides have gained great interest due to their numerous biological and biofunctional activities reported such as antioxidant, antihypertensive, antimicrobial, and metal-chelating properties[1]. Biofunctional peptides, as metal-chelating peptides (**MCPs**), are derived either from matrices of animal origin or from vegetable[1].

In a bioeconomy strategy, the protein sources from plant and agro-industrial co-products have currently gained significant interest due to their low environmental impacts production, high protein content, and potentially high-added value[2].

Objectives and stakes :

This PhD thesis aims to investigate the use of vegetable and fish processing co-product proteins for the production of peptide hydrolysate and the discovery thereof of MCPs

Methodology :

Production of protein isolated from agro-industrial co-products. Tilapia scale flour was prepared according to the literature [3]. Then, demineralization process and hydrothermal extraction were carried out to obtain gelatin protein. The extraction conditions of gelatin protein were optimized using a fractional factorial design, which involved 4 factors: the solvent- to-solid ratio of extraction (A, 2-10 mL/g), the extraction time (B, 1-3 h), the temperature (C, 65-85 °C) and the ultrasound time (D, 0-60 min). The protein percentage (%), the free amino groups (**FAG**, mmol Eq G/g) and the protein extraction yields (**PEY**, %) were determined.

According to the best conditions obtained for protein extraction, Tilapia scale gelatin was hydrolyzed using three enzymatic treatments: Alcalase® alone (**Alc**), Flavourzyme® alone (**Flav**) or a sequential treatment Alcalase® followed by Flavourzyme® (**Alc+Flav).** Physico-chemical, and biofunctional characterization (*i.e.,* metal-chelating, antioxidant, antihypertensive, and antimicrobial activity) were carried out for all samples.

Illustration 1 : Optimization of gelatin and TSGH properties

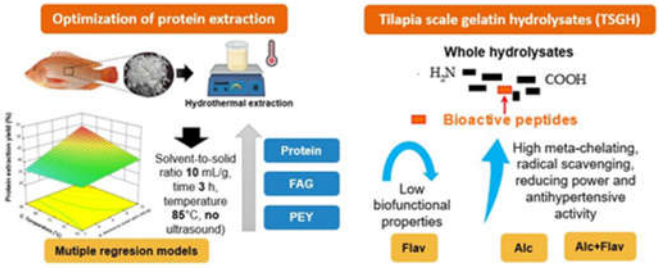


Illustration 2: Antioxidant properties of TSGH and controls

Sample	TEAC (µmol TE/g)	ABTS EC_{50} (mg/mL)	DPPH EC_{50} (mg/mL)	Reducing power EC_{50} (mg/mL)
Alc	71.89 ± 2.32[a]	0.17 ± 0.0051[a]	20.97 ± 0.76[a]	11.33 ± 0.60[a]
Flav	61.66 ± 3.28[b]	0.19 ± 0.01[b]	n.d.	13.45 ± 1.10[b]
Alc+Flav	74.79 ± 1.87[a]	0.15 ± 0.004[c]	18.61 ± 0.97[b]	7.53 ± 0.38[c]
Carnosine	28.37 ± 2.20[c]	0.40 ± 0.008[e]	5.82 ± 0.23[c]	1.26 ± 0.16[d]
Trolox®	--	0.04 ± 0.0007[f]	0.006 ± 0.0003[d]	
Ascorbic acid	--	--	--	0.005 ± 0.0003[e]

Main results

The protein percentage of gelatin extracts varie slightly (95.41-99.20%), and is in agreement with isolate protein content (>85%)[4]. The solvent-to-solid ratio, the temperature, and their interaction have the most significant effect on the FAG, and on PEY. Concerning hydrolysates, the sequential treatment (Alc+Flav) shows the highest DH value (29.74%), followed by the Alc (19.70%), and Flav (4.35%) ones. Hence, the Alcalase® has a higher proteolytic activity towards Tilapia scale gelatin, compared to Flavourzyme®. Alc and Alc+Flav hydrolysates show the highest biofunctional properties (metal-chelating, TEAC, ABTS, DPPH and reducing power, and antihypertensive activities), which depend of their constituting peptides, and especially their size, amino acid composition and sequences. Inversely, for all of them, the Flav hydrolysate show the lowest values, in relation to the lowest DH and thus, the presence of bigger peptides. Both hydrolysates offer an effective strategy for obtaining metal-chelating peptides.

References :

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[3] Tu *et al.,* **2015**. *FJ. Food. Sci. Technol*. 52(4): 2166-2174

[4] Zhang *et al.,* **2019**. *Molecules*. 24 (16): 1-14

2022

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

Pilar Chavez Linares (1st year)

Isabelle Chevalot, Sandrine Hoppe

Axe BIOPROMO | Ecollant SAS

Keywords : : biocatalysts, extrusion, polyamide 6,6; elastane; textile recycling

General context, scientific issues :

Every year, more than 130 million pairs of polyamide tights (better known as "pantyhoses") are sold in France. In general, these tights are relatively short-lived products. In fact, in more than 70% of cases, the tights do not last more than six uses, and even only three uses for more than 40% of users (according to a survey report by the HOP association published on the website *www.halteobsolescence.org*). This fast consumption generates a significant amount of waste: it is estimated that 104 million used tights are thrown away in France each year, which represents 7,315 tons of wastes.

The complex composition of tights makes difficult the revalorization of the components such as nylon and elastane. A closed-loop recycling process consisting of remaking tights from used tights would make it possible to get out of this linear "produce, consume, throw away" model. The process used to carry out this depolymerization is based on an enzyme-catalyzed cleavage of the polyamide chains in the aqueous phase, in order to limit as much as possible, the impact on the environment.

Objectives and stakes :

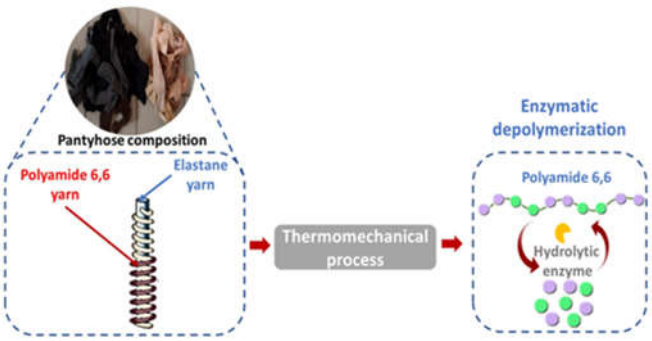
The main objective of this project is the development of a green process for the hydrolysis of polyamide 6,6 which is one of the main polymer's component of pantyhose.
The study will include a laboratory scale experimental work on the selected processes (thermomechanical and enzymatic) in order to decrease the crystallinity degree of polyamide 6,6.
Several hydrolases enzymes will be used for the enzymatic hydrolysis of raw materials (polyamide, elastane and yarn blends).

Methodology :

A first approach will be focused on the understanding of the hydrolysis mechanisms of polyamide 6,6 and polyurethane catalyzed by enzymes and the possible impact of dyes additives on the enzymatic activity. The production of oligomers and monomers constitutive of polyamide 6,6 will be the key to select the optimal conditions of the various treatments implemented.

To this end, analyses of the primary amino groups are established [1] and the residual material will be characterized by different methods: thermal analysis (DSC) and (TGA), rheological and gel permeation chromatography (GPC) in order to determine its depolymerization degree [2]–[4] . In a second approach, the coupling of thermomechanical and enzymatic treatments will be considered. A schematic representation of the process is shown in the illustration 1

Illustration 1 : Thermomechanical and enzymatic processes for pantyhose recycling



Expectations

The process will be developed in a pre-industrial stage perspective. An appropriate enzymatic system will be selected in order to depolymerize the polyamide 6,6. It is expected to optimize a type of process with low energy consumption and the use of enzymes as reaction catalysts in aqueous media.

References :

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

2022

Research subject : Development of new anti-microbial materials for hygiene and food safety

Tatevik Chilingaryan (3rd Year)

Dr. Céline Frochot, Dr. Benoît Habermeyer

Axe BIOPROMO | PorphyChem

Keywords : Photodynamic inactivation, Photosensitizer, Singlet oxygen, Bacteria, Virus

General context, scientific issues :

More than 100 years ago it has been known that microorganisms can be killed using nontoxic dyes known as photosensitizers (PS), combined with light. In 1900, Raab reported successful inactivation of Paramecium caudatum by acridine [1]. He observed that acridine is efficient during the day under light conditions and kill these microorganisms, while in darkness there is no effect. One of the reasons why PDI has been forgotten for many years was due to the discovery of antibiotics and their large application and use ranges.

However, conventional antibiotics are no more efficient, and the problem of increased resistance developed by bacteria, fungi, viruses, lead to find new methods and develop already existing ones, such as PDI. One of the challenging advantages of PDI is the ability to oxidize different biomolecules. Also, the same photosensitizer is able to destroy viruses, bacteria, yeasts, fungi and protozoa[2-6]. Another important advantage of PDI over conventional antibiotic treatment is that no microbial resistance has been reported so far. PDI is a combination of photosensitizer (PS) and light to generate cytotoxic reactive oxygen species (ROS) that kill bacteria and viruses

Objectives and stakes :

Our goal is the development of new antimicrobial films[7] for PDI for application in hygiene and food safety. These films can be introduced to any kind of surface in order to kill bacteria and prevent its growth on the surface. The objective consists in several steps:

- Synthesis of PS (porphyrins, phthalocyanines and chlorins)

Study of Influence of counteranions and symmetry on electrochemical properties of water-soluble porphyrins.

- Incorporation of PS into film: Our main candidate for film is polyethylene terephthalate (PET)

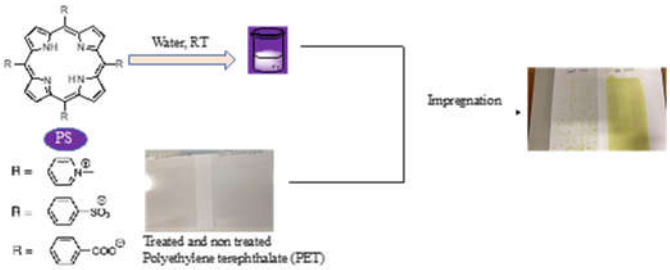
Photophysical studies of PS

- Antimicrobial studie

Methodology :

- Synthesis of organic molecules
- Characterization by UV-Vis, MS, HPLC phase normal and reverse phase, ^{1}H RMN, Fluorescence and Singlet Oxygen production measurements.

Illustration : Fabrication of antimicrobial films



Main results

- Synthesis of second-generation photosensitizers has been released.
- Successful incorporation of porphyrins into polyethylene terephthalate (PET)
- Photophysical properties of PS, PS+film have been investigated
- Singlet oxygen production for some of PS+film have been demonstrated

References :

[1] O. Raab, *Zeit Biol*., **1900,** *39524-39546***.**

[2] M.Perlin, J. C. H. Mao, E. R. Otis, N. L. Shipkowitz, R. G. Duff, *J. Antiviral Res.,* **1987**, *7*, 43-51.

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[4] N. Yeshayahu, H. M. Wexler, S. M. Finegold. *J. Curr. Microbiol.,* **1994**, *29*, 125-131.

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[6] A. C. Giese, *J. Phis. Zool.*, **1953**, *26*, 1-22. [7] L. Jiang, C. R. R. Gan, J. Gao, X. J. Loh, *Small* **2016**, *12*, 3609-3644.

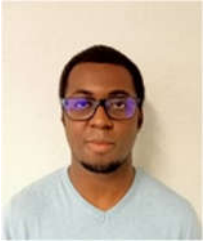
2022

Research subject : Development of an innovative bioleaching process for the treatment of limonitic nickel laterites – BIONICKEL

Samir Daniel (1st year)

Eric Olmos, Anne-Gwénaëlle Guezennec

Axe BIOPROMO



Keywords : Bioprocess, nickel, cobalt, laterite, reductive bioleaching.

General context, scientific issues :

Limonitic nickel laterite are oxidized ores mainly composed of goethite (FeOOH) which host up to 2 % of nickel and 0.5 % of cobalt. Traditionally, they are processed through Pressure Acid Leaching (PAL), which consists in dissolving goethite at high temperature (220 to 270 °C, 60 bars) in sulphuric acid in an autoclave. Unfortunately, PAL plants have often proven to be very costly, plagued with technical challenges. Recently, the bacterial catalysis of goethite dissolution have been highlighted using iron reductive acidophilic microorganisms like *Acidithiobacillus (At.) ferrooxidans* [2]:

$$FeOOH \rightleftarrows Fe^{3+} \xrightarrow{bacteria} Fe^{2+}$$

They are able the breath ferric iron in anaerobic condition while oxidizing sulphur and using CO_2 for their growth in less energy-consuming conditions (30°C, atmospheric pressure) than PAL processes [2]:

$$6Fe^{3+} + S^0 + 4H_2O \xrightarrow{bacteria} 6Fe^{2+} + SO_4^{2-} + 8H^+$$

However, the optimal operating conditions for coupling biological activity and chemical dissolution reactions remain to be determined.

Objectives and stakes :

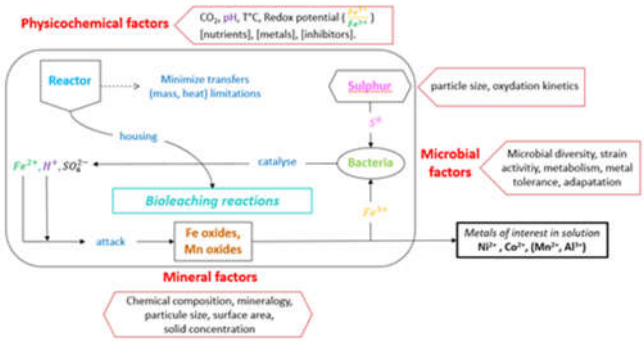
The objective of this work is to develop a continuous process at pilot scale, based on the reductive bioleaching of goethite by *Acidithiobacillus* species (*At. ferrooxidans* in our case), to extract nickel and cobalt from limonite nickel laterites of New Caledonia. This study is divided into three steps, using shake flasks and bioreactors from 2L to 51L:

* The determination of experimental conditions that favour bacterial growth coupled with iron reductive activity.
* The identification of the rate-limiting factors of limonite leaching, especially concerning the mineral composition of the ore and bacterial growth inhibition.
* An optimization of operating parameters in a continuous bioreactor to promote iron bio-reduction performance, metals dissolution rates and reduce chemical reagents consumption.

Methodology :

*Iron reduction kinetics: Redox monitoring using an Ag/AgCl redox probe and a correlation with the Fe(III)/Fe(II) ratio [3].
*Sulphur oxidation: By IEC of sulphate.
*Leaching kinetics: By SAAF and MP-AES analysis of the pregnant leaching solution and mass balance with mineral composition.
*Bacterial growth: By Thoma cell counting method.
*Gas-liquid mass transfer coefficient, oxygen and carbon uptake rates: using an oxygen probe or an oxygen sensor spot.

Illustration : Reductive bioleaching of limonitic laterite scheme and key operation factors.



Perspectives

The main challenge to overcome in this study is to obtain a culture of *At. ferrooxidans* with sufficient growth and iron reductive rates in anoxic condition. At present, the reductive bioleaching of nickel laterites has been conducted in two steps: aerobic growth of bacteria on sulphur followed by the anaerobic reductive bioleaching step with the ore [4]. However, it has been highlighted that *At. ferrooxidans* can lose the iron reducing ability after prolonged aerobic cultivation on sulphur but can regain it after one sub-culture on ferrous iron [5].

In order to investigate this matter, the growth kinetics of *At. ferrooxidans* will be studied in shake flasks of 250 mL at pH 1,8 and 30°C, using ferrous iron or/and sulphur as substrates in aerobic conditions. The iron reducing ability of different subcultures will be tested for ferric iron reductive (anaerobic) afterwards to determine the best ferrous iron/sulphur ratio to keep the iron reducing ability.

References :

[1] Sevin, Brice. 2014. « Cartographie du régolithe sur formation ultrabasique de Nouvelle-Calédonie : Localisation dans l'espace et le temps des gisements nickélifères ». Theses, Université de la Nouvelle-Calédonie.

[2] Hallberg, Kevin B., Barry M. Grail, Chris A. du Plessis, et D. Barrie Johnson. 2011. « Reductive Dissolution of Ferric Iron Minerals: A New Approach for Bio-Processing Nickel Laterites ». Minerals Engineering 24 (7): 620–24.

[3] Yue, G., Guezennec, A.-G. and Asselin, E. (2016) 'Extended validation of an expression to predict ORP and iron chemistry: Application to complex solutions generated during the acidic leaching or bioleaching of printed circuit boards', Hydrometallurgy, 164, pp. 334–342.

[4] Malik, Luise, et Sabrina Hedrich. 2022. « Ferric Iron Reduction in Extreme Acidophiles ». Frontiers in Microbiology 12.

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2022

Research subject : Application of the PAT approach for on-line monitoring and control of functional parameters of animal cells cultured in bioreactors

Aurelia Denner (4th year)

Emmanuel Guedon, Bruno Ebel

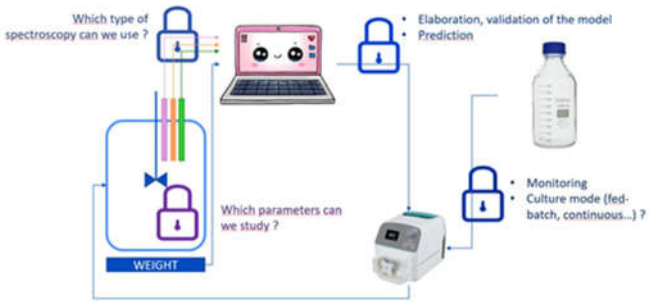
Axe BIOPROMO

Keywords : Chinese Hamster Ovary, Process Analytical Technology, Monoclonal Antibodies, Raman Spectroscopy, Chemometrics, Partial Least Square Regression

General context, scientific issues :

Monoclonal Antibodies (mAbs) and more specifically Immunoglobulins G (IgG) are the most commonly utilized antibodies for therapeutic use. They are produced by Chinese Hamster Ovary (CHO) cells in animal cell culture process. One of the main challenges in such process is to guarantee the quality of the product at large scales. In recent years, industries focused on Process Analytical Technology (PAT) in order to achieve real-time monitoring of cell culture and to make possible control of bioprocesses using performant technologies such as near infrared, dielectric or Raman spectroscopies. Raman spectroscopy is commonly used in industry [1] because it is non-destructive and easy to use through chemometric approaches.

Illustration : Methodology of CHO cell culture process



Objectives and stakes :

Cell cultures are operated in 2L bioreactors. Seven batch and twenty-three fed-batch cultures were realised in order to calibrate models using Raman and dielectric spectrometers. Spectral data need to be pre-processed before making operational models. That is why an optimizing/improving program were developed. For types of pre-processing were studied: Savitzky Golay filter, Standard Normal Variate scaling, simple Normalization and Multiplicative Scatter Correction. More than six thousand combinations/pre-processing were tested for each studied parameter (Viable Cell Density (VCD), glucose and lactate). The model performances were evaluated by various statistic parameters including Root Mean Square Errors and regression coefficients. Finally, these models will be used to calculate kinetic parameters such as cell specific growth rate (μ), specific product formation rates (π) and/or substrate consumption rates (η)

Methodology :

2L scale bioreactor cultures: Thirty bioreactors were performed implemented with on-line analysers such as Raman, dielectric, pH, O_2 and temperature probes. Three types of process mode were studied: batch, fed-batch with manual adding and fed-batch with a pump.

Batch cultures: 2L scale bioreactor with 1.5 working volume. Only concentrated glucose and glutamine solutions were added at the end of the culture in order to extend it.

Manual fed-batch cultures: Industrial concentrated solutions (feeds) were added from the third day of culture. Required volumes were calculated thanks to concentration balances.

Fed-batch culture with pump: Concentrated initial culture medium were added. The working speed of the pump were calculated for each sample and adjusted calculating the feed flow rate.

Main results

Chemometrics and modelling: Partial Least Square regression was compared with Regressions Trees, Support Vector Machines, Gaussian Process Regression Models (GPR), Ensembles of Trees and Neural Networks for the monitoring of VCD and metabolite concentrations. Results showed that GPR is more reliable and allows the best prediction of these process parameters. Then it was possible to calculate precisely μ and $Y_{X/S}$ in real-time, that was not possible with the PLS regression only.

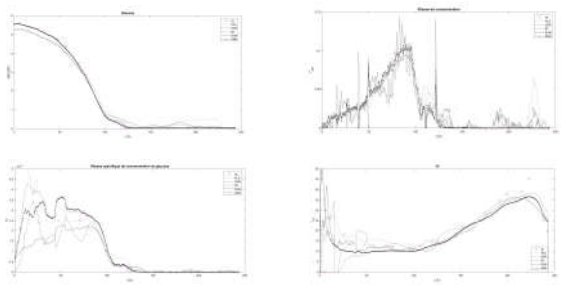


Figure – Estimation of glucose concentration, r'''glc, η and $Y_{x/s}$

Fed-batch cultures: In future experiments, the best models will allow to calculate the feed flowrate of the fed-batch process, resulting in a good regulation that will ensure the maintenance of optimal performance of the process. It will be possible to compare achievements of monitored/controlled processes with those operated manually.

References :

References

[1] Whelan et al. In Situ Raman Spectroscopy for Simultaneous Monitoring of Multiple Process Parameters in Mammalian Cell Culture Bioreactors. Biotechnol. Prog. 2012, Vol. 28, No. 5

[2] Lee G.M. and Koo J. Osmolarity effects, Chinese hamster ovary cell culture. Encycloperdia of Industrial Biotechnology: Bioprocess, Biosepara-tion, and Cell Technology. 2010

2022

Research subject : New lipophilic or amphiphilic derivatives of bio-based phenolic compounds with antioxidant, anti-inflammatory and / or anti-proliferative properties

Georges Eid (4th year)

Christine Gerardin, Catherine Virot

Axe BIOPROMO | LERMaB

Keywords : Polyphenols, wood extractible, hemisynthesis, enzymatic catalysis, self-assembly, anti-oxydant, molecular modelling

General context, scientific issues :

The decrease in petrochemical resources, easily accessible, has generated, over the past decade, a growing interest in the use of raw materials of renewable origin. Bio-sourced chemistry first developed strongly around annual agro-resources. The project fits in that context of valorization of wood by-products, through the use of wood secondary metabolites. Many medicinal plants contain large amounts of antioxidants such as polyphenols, where the interest in valorising those compounds.

Objectives and stakes :

The main objective is the valorization of phenolic extractable. These compounds are indeed of interest because of their anti-oxidant and anti-radical properties.

In order to valorize these compounds, their structure will be selectively modified by chemical and enzymatic way in order to exacerbate their antioxidant properties, their anti-inflammatory and / or anti-proliferative activity by the modulation of their hydrophilic / hydrophobic balance, in particular to facilitate their passage through the biological barriers and, secondly, to facilitate their formulation by providing them with self-assembly properties. Since the properties and biological activities of the products are directly related to their structure, particular attention will be paid to understand and control the regio- and chemo-selectivity of the reactions by molecular modelling. The antioxidant and self-assembly properties of the derivatives obtained will be characterized and the biological properties such as anti-free radicals or anti-proliferative can be evaluated

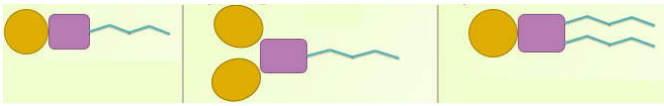
Methodology :

Flavonoids' acylation will be done by chemical and enzymatic ways in order to obtain tri-modular amphiphilic compounds. Chemical acylation will be done on aglycone flavonoids with protection/deprotection to target the aliphatic hydroxyl group. On the other hand, enzymatic acylation will cover glycosylated flavonoids using lipases from *Candida antarctica*. The obtained products will be characterized by NMR, IR and mass spectroscopy, then their antioxidant, antiproliferative and self-assembly properties will be tested

Illustration : Tri-modular compound

Main results

Chemical of catechin with different amino acids and fatty acids, allowed us to obtain three types of compounds. The first type of molecule has one polar head (catechine), one junction module (alanine) and one hydrophobic chain (fatty acid). The second type of molecule has two polar heads, one junction modul (glutamic acid) and one hydrophobic tail. And finally the last type of molecule has one polar head, one junction module (lysine) and two hydrophobic tails.



Enzymatic acylation of rutine and naringin with an excess of 6 fatty acids in a very dry media using lipase B of *Candida antarctica* allowed us to obtain products with a very high yield and acylation with di-acids using the same enzyme, allowed us to obtain products as well.

The physicochemical properties of the obtained compounds showed self-assembly properties for the compounds with fatty acids but not with the glycosylated compounds and that's due to their high solubility.

Also all the compounds showed good antioxidant activity with DPPH and inhibition of the methyl linoleate. A correlation exists between the antioxidant activity and the fatty acid length chain. When the chain length increases the activity decreases.

References :

[1] Amy Yi Hsan Saik et al., 2017, Biotechnology Letters, volume 39, 297-304.

[2] Shan Hong et al., 2016, Food Chemistry, volume 197, 415-421.

2022

Research subject : Methodologies for screening metal-chelating peptides for their antioxidant properties

Sarah El Hajj (PhD Defended on 22nd March 2022)

Laetitia Canabady-Rochelle, Caroline Gaucher

Axe BIOPROMO | CITHEFOR

Keywords : : Screening, ferroptosis, metal-chelating peptides, soy protein hydrolysates.

General context, scientific issues :

Ferroptosis is a recently defined type of cell death, whose main feature is lipid peroxidation catalysed by iron-overload and is reported in diseases such as Atherosclerosis. To date, there is no model of ferroptosis based on cardiovascular cells to test molecules able to inhibit ferroptosis. Metal-chelating peptides (MCPs) can reduce cellular oxidative stress caused by metal ions overload. Hydrolysates constitute potential sources of metal-chelating peptides that could be used for reducing ferroptosis.

Objectives and stakes :

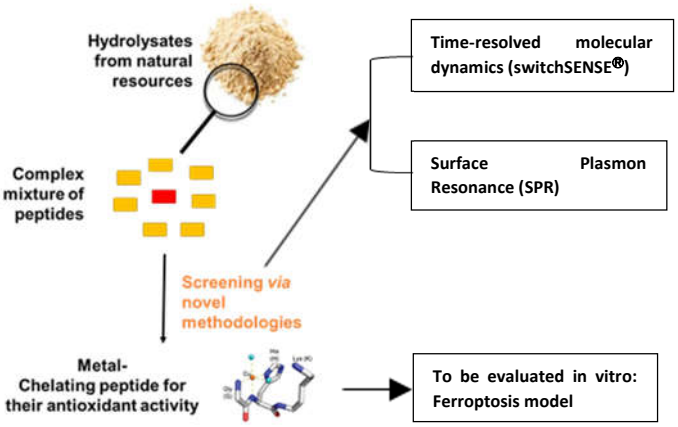
The objective of our study is to screen metal-chelating peptides present in soy protein hydrolysates (SPHs) using novel screening techniques that overcome the limitations (*ex*. time consuming, fastidious, unspecificity, *etc.*) of the empirical approach usually employed to screen MCPs. On the other hand, we aim to develop a model of ferroptosis on primary human smooth muscle cells (HAoSMC) to test MCPs as drug candidate to limit the development of atherosclerosis.

Methodology :

Soy protein hydrolysates (SPHs) were produced under various hydrolysis conditions. Three enzymes were used individually (Alcalase®, and Protamex®) during 1 or 3 h and sequentially (Alcalase® 1h followed by Flavourzyme 2h ®, and Protamex 1h followed by Flavourzyme 2h). The hydrolysates were then ultrafiltrated through 1kDa membrane.

Before ultrafiltration, the whole hydrolysates were examined by dynamic biosensor switchSENSE®, a screening method applied for the first time on MCPs. After ultrafiltration, the binding affinity of peptides hydrolysate to Ni^{2+} was analysed by SPR using Biacore X100 instrument equipped with NTA sensor chips.

Illustration : Aim of the PhD



Main results

Time-resolved molecular dynamics (switchSENSE®) has proven to be very sensitive for detecting the presence of MCPs in peptide hydrolysates. This methodology is able to categorize the metal-chelating activities of the studied hydrolysates according to the enzymatic treatment or the protein source: Tilapia viscera or soy isolates.

Screening by SPR has revealed the association and dissociation phases for MCPs binding to Ni^{2+} in a concentration dependent manner. Thanks to its sensitivity we were able to conclude that sequential hydrolysis of soy protein isolate by Alcalase® followed by Flavourzyme® was the best treatment to produce MCPs.

In cellular experiments, the ferroptosis model is validated by the depletion of GSH intracellular concentration upon Erastin incubation since, as a system Xc- inhibitor, Erastin, is responsible for the decrease of cysteine entry into the cells, which is a precursor for GSH synthesis, and by lipid peroxidation by Erastin and ferric citrate incubations. The rescue model is validated by lipid peroxidation upon the addition of

References :

[1] El hajj *et al.,* (2022) J. Argric. Food Chem. **69 (31)** 8819-8827

[2] El Hajj *et al.,* (2022) Food Chem. *In submission*

Acknowledgements. This PhD was supported by the "Impact Biomolecules" project of the "Lorraine Université d'Excellence" (Investissements d'avenir – ANR project number 15-004).

2022

Research subject : Study of the solvation of biomolecules and lipases in deep eutectic solvents for biotechnological applications

Rabih Elia (2nd year)

Latifa Chebil, Walid Harb

Axe BIOPROMO

Keywords : Deep eutectic solvents, molecular dynamics, lipases, force fields, ionic liquids, biocatalysis, Hydrogen bonds

General context, scientific issues :

For the last two decades, research on ionic liquids has increased dramatically as chemistry trends are pointing towards "green" solvents. First described in 2003 [1], deep eutectic solvents (DESs) have emerged as the green solvents of choice considering their properties, low melting point, ease of synthesis and tunability to a wide array of biochemical applications. Among these, deep eutectic solvents of the choline chloride analogues have attracted much attention during the past decade for their capability to dissolve biomolecules and their use as a medium in reactions catalyzed by enzymes. Experimental techniques are costly and limited in their ability to analyze reactions parameters, As such; computational studies have become a trend in the study of DESs and their interactions with different biomolecules. However, adequate force fields parameters need to be adapted correctly in order to have a precise predictive model that can then be validated by experimental techniques.

Objectives and stakes :

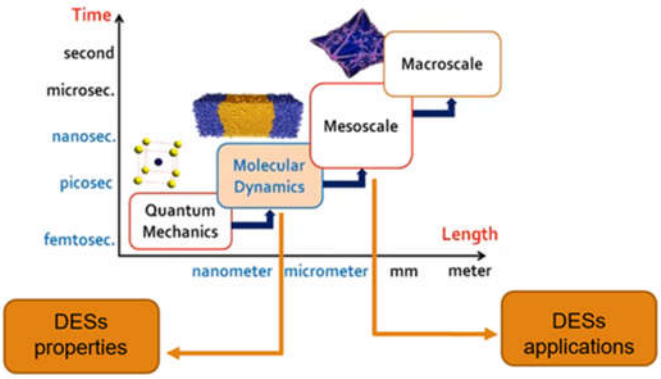
Bibliographical review on force fields advances, publications and parameters optimizations regarding DES systems.
Molecular dynamics on DESs/amino-acids systems to understand the interactions on a molecular scale and validation with experimental techniques.

Methodology :

The MD simulations are carried out using GROMACS software. Systems studied are 1:2 mixtures of DESs:
- Reline (choline chloride + urea) + glycine at 0%, 5% and 10% wt
- Glyceline (choline chloride + glycerol) + glycine at 0%, 5% and 10% wt
- Ethaline (choline chloride + ethylene glycol) + glycine at 0%, 5% and 10% wt

OPLS AA force field [2] and GAFF1.21 [3] are used in these simulations. A 10000-step energy minimization is performed followed by two simulations; the first one for 10 ns for equilibration and the final one for 50 ns for production

Illustration : Exploration of DESs using MD simulations



Main results

A bibliography review was prepared. It comprises of sections briefly describing DESs types, properties and applications and pointing to the current state of scientific research. The last section intricately details the work done of the exploration of DESs system via force fields and presents an exhaustive chronological table on publications and studies which explored DESs systems with molecular dynamics along with the evolution on force fields parametrization.

MD simulations results are compared with literature data and previous experimental data. Some physicochemical properties (density, viscosity, surface tension) and structure analysis data (RDFs, coordination numbers, H-Bonds analysis) are calculated. These results serve as a baseline for the choosing of an adequate force field to develop next simulations with different amino acids and eventually build a DES-biomolecule system.

References :

[1] Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures.

[2] Doherty, B., & Acevedo, O. (2018). OPLS Force Field for Choline Chloride-Based Deep Eutectic Solvents. Journal of Physical Chemistry B, 122(43), 9982–9993.

[3] Chaumont, A., Engler, E., & Schurhammer, R. (2020). Is Charge Scaling Really Mandatory when Developing Fixed-Charge Atomistic Force Fields for Deep Eutectic Solvents? Journal of Physical Chemistry

2022

Research subject : study of cells adhesion to microcarriers for cell culture process development

Gaye Ibrahima (4th year)

CHEBIL Latifa, GUEDON Emmanuel

Axe BIOPROMO

Keywords : mesenchymal stem cells, adhesion, detachment, molecular and mesoscopic dynamics, interaction, microcarrier

General context, scientific issues :

Stem cells are at the heart of the recent development in cell therapy and tissue engineering(Carrion and Figueroa, 2011). Human mesenchymal stem cells (hMSC) are among the most widely studied stem cells. However, these cells are present in a very limited amount in the body. Consequently, the development of a high-performance process for the expansion of hMSC is essential to meet therapeutic needs (Martin, 2016).

Objectives and stakes :

The main objective is to develop original approaches combining multi-scale modeling and experimentation to improve the performance of the hMSC expansion process. This will involve: i) improving the understanding of the phenomena that govern the adhesion and stalling of cells on controlled surface (microcarriers) by molecular / mesoscopic modeling; ii) streamline the choice and formulation of microcarriers; iii) provide the necessary data (adhesion forces, shear forces) to refine CFD simulations at the macroscopic scale of the bioreactor.

Methodology :

1. Identification of membrane phospholipids: to find out the main phospholids present in the membrane of mesenchymal stem cells, we performed a lysate analysis of membranes by liquid chromatography coupled with mass spectrometry (LCMS).
2. Study of cell / microcarrier systems at the molecular level: First, the membrane is considered as a simple bilayer of phospholipids with different proportions of PC, PG and PE. Two types of microcarriers surfaces are studied (Cytodex1, Plastic +). Molecular dynamics applied to these systems provides adhesion work, van der Waals interactions, electrostatic forces and hydrogen bonds. The results obtained are compared to adhesion forces measured by atomic force microscopy (AFM the).

Membership work calculation formula

$$W_{ad} = \frac{1}{A}(E_{\mu porteur} + E_{membrane} - E_{\mu porteur+membrane})$$

3. AFM measurement condition: contact time of 5 s, 10 s and 15 s, , used microcarrier material of plastic, cells 48 hours after trypsination.

Illustration : adhesion and modeling study

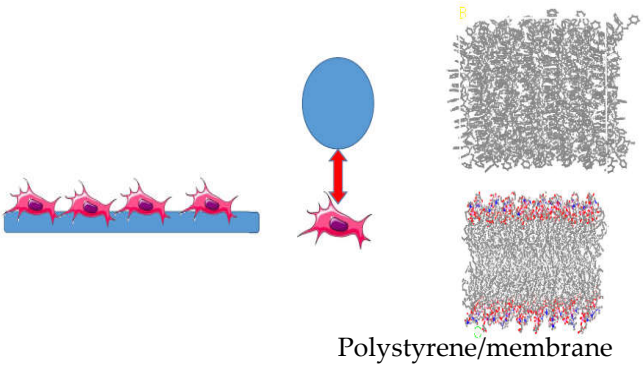
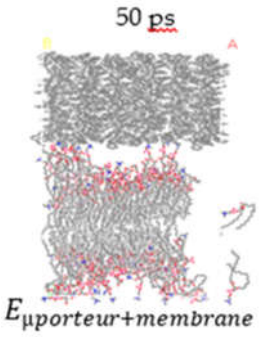


Figure 1 study of work adhesion by AFM and by molecular dynamics

Main results

LCMS analysis shows that the phospholipids predominantly present in the membrane of MSCs are PC, PG and PE with a different distribution

Table 1 result of the adhesion work between MSC membrane and microcarriers by modeling and average of experimental measurements



DM	W_{ad}DEAE/ membrane (J)	W_{ad} Polystyrene/membrane (J)	AFM measure (J)
1	$1,96.10^{-16}$	$1,45.10^{-16}$	
2	$2,01.10^{-16}$	$1,42.10^{-16}$	
3	$1,99.10^{-16}$	$1,35.10^{-16}$	
average	$1,99.10^{-16}$	$1,41.10^{-16}$	$7,99.10^{-15}$
St dev	$2,45.10^{-18}$	$5,02.10^{-18}$	$2,20.10^{-15}$

Table 1 showed that the work of adhesion values, obtained by molecular modelling, between the membrane and the two types of support are $1,99.10^{-16}$ J and $1,41.10^{-16}$ J for with DEAE and polystyrene, respectively. The measured work of adhesion increase within the time of measurements, with an average value of $7,99.10^{-15}$J.

References :

Carrion, F.A., Figueroa, F.E., 2011. Mesenchymal stem cells for the treatment of systemic lupus erythematosus: is the cure for connective tissue diseases within connective tissue? Stem Cell Res. Ther. 2, 23. https://doi.org/10.1186/scrt64

Martin, C., 2016. Étude des procédés d'amplification de cellules souches mésenchymateuses hu

2022

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

Laureline Gennesseaux (2nd year)

Catherine Humeau and Yann Guiavarc'h

Axe BIOPROMO

Keywords : enzymatic process ; aminoacylase ; N-acylation ; enzyme structure-fonction relationships ; production of recombinant enzymes ; molecular modelling

General context, scientific issues :

Acylated derivatives of amino acids and peptides are interesting compounds for many industrial applications due to their emulsifying and foaming properties. The structure of these biobased compounds consists of one hydrophilic amino acid or peptide unit and one fatty acid chain from vegetable oils. 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. The main limitation to their use is the lack of knowledge about their structure and their catalytic mechanism

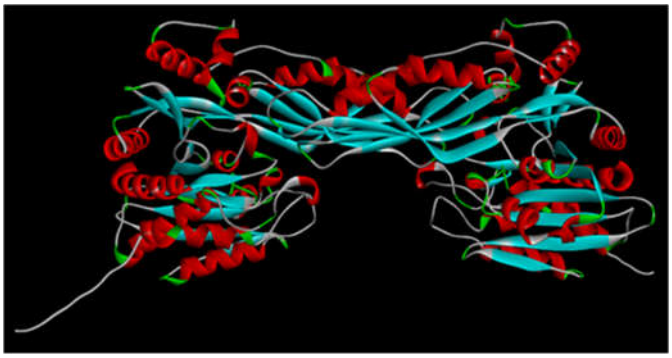
Objectives and stakes :

This project aims at developing a selective, efficient and eco-friendly bioprocess for the production of 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.

Methodology :

A combined experimental/numerical approach is implemented, using experimental tools as molecular biology, enzymology, process engineering and molecular modeling tools as docking simulations and homology models. The study is organized according to three main issues: (1) intensifying the production and the purification of the four recombinant amino-acylases from S. ambofaciens in order to produce sufficient quantities of pure enzymes for cristallographic studies (2) studying the catalytic mechanism of aminoacylases. The structure of the enzymes will be determined using homology models and then compared to the structures obtained by crystallography analyses. Enzyme-substrates binding modes will be determined with molecular docking simulations (3) determining the optimum operating conditions for each enzyme in different reactor configurations in order to design enzymatic N-acylation bioprocesses.

Illustration : Homodimeric model of SamAA obtained with AlphaFold2, basing on the protein sequence



Main results

The study began with the Sam_AA protein, which catalyzes the N-acylation reaction at the α position of amino acids. This selectivity is rare in the world of enzymes. The Sam_AA enzyme is mainly produced in the form of insoluble aggregates called inclusion bodies in the *E. coli* bacterial system. Many operating parameters have been tested to solve this problem, without success. It is currently planned to work on inclusion bodies with a refolding strategy, with the aim of increasing the amount of Sam_AA soluble form. Similar production work is in progress with the Sam_ELA enzyme catalyzing the N-acylation reaction at the ε position of lysine. In parallel to this experimental approach, molecular modeling simulations were performed. Homology modeling is a computer prediction method for determining the 3D structure of a protein based on its amino acid sequence and its homology with one or more templates of known structure. After the identification of the templates, the performances of different homology modelling tools (Modeler, Swiss Model and AlphaFold) were compared and a model of the 3D structure of Sam_AA was developed. This model will be optimized and then used for molecular docking simulations in order to study the enzyme/substrates binding modes and the catalytic mechanism of the enzyme.

References :

Dettori et al. Micropor Mesopor Mat, 2018, 267 : 24-34
Dettori et al., Eng Life Sci, 2018, 18(8) : 589-599
Bourkaib et al., Enzyme Microb Tech, 2020, 137
Jumper et al., Nature, 2021, 596 : 583-592

2022

Research subject : Development of a bioprotection process by solid state fermentation applicable in the barley-malt-beer sector

Kpèho Eusèbe GNONLONFOUN (3rd year)

Michel FICK, Emmanuel RONDAGS

Axe BIOPROMO | IFBM

Keywords : Barley; pathogenic fungi; mycotoxins; malting; bacterial control; bioprotection

General context, scientific issues :

Pathogenic fungi represent a generic problem for cereals, including barley, as they can produce a number of thermo-stable toxic metabolites such as mycotoxins that contaminate plants and food products, leading to serious health issues for human and animals and causing significant losses in global food production. In addition, mycotoxins represent a significant technological concern for the malting and brewing industries, as they may affect the quality and safety of raw materials (barley and malt) and final products (beer). Moreover, this situation is worsening due to the highly variable climatic conditions that favor microbial development and the societal desire to reduce the use of phytosanitary products, including fungicides. In this complex environmental, legal and economic context for agriculture in general and more specifically for the barley-malt-beer sector, the use of technological microorganisms to reduce the development of spoilage fungi and the production of mycotoxins, is considered to be a potentially interesting and natural solution for protection against these fungi, given that several studies have shown their effectiveness for this purpose [1, 2].

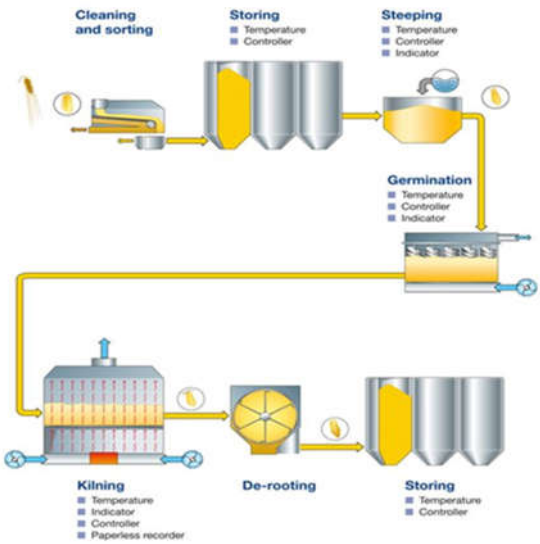
Objectives and stakes :

The main goal of this project is to develop an antifungal biocontrol process applicable in malting in order to maintain and improve the sanitary and technological quality of French malts. This will be done by using technological bacteria, isolated from infection-resistant barley cultures, that are able to reduce the development of pathogenic fungi and the associated mycotoxin production.

Methodology :

The experimental approach consists of i) co-culturing bacterial and pathogenic fungal strains in solid and liquid media to access the growth kinetics of these microorganisms and to evaluate the impact of these bacteria on fungal growth and mycotoxin production; then ii) the results will be used to carry out a micro-malting process in order to develop the aforementioned process, and iii) the technological and sanitary properties of the generated barley malts will finally be evaluated in order to validate the biocontrol process developed

Illustration : The malting process



Main results

Our results highlight the ability of a novel bacterial strain isolated from barley kernels, *Erwinia gerundensis*, to inhibit the growth of fungal species and to reduce their toxigenic potential. *E. gerundensis* exhibited a significant fungistatic activity against pathogenic fungi by reducing their growth and their mycotoxin production by 60 to 100%. Based on these results, our study supports the use of *E. gerundensis* as a biocontrol agent in strategies aiming at reducing the presence of pathogenic fungi and mycotoxins in cereal-based products, or as a food and feed supplement for the biodetoxification of mycotoxins [3]. Further experiments are underway, for the development of a bioprotection process based on *E. gerundensis*, applicable during the malting process. It is expected to make it possible to guarantee an irreproachable hygienic and technological quality of the malt obtained from barley. The use of this process will also contribute to the reduction of contamination levels of malting plant effluents.

References :

[1] Sadiq *et al.* (2019). Lactic Acid Bacteria as Antifungal and Anti-Mycotoxigenic Agents: A Comprehensive Review. *Compr. Rev. Food Sci. Food Saf.*, 18: 1403-1436.

[2] AFSSA. (2009). Rapport final : Evaluation des risques liés à la présence de mycotoxines dans les chaînes alimentaires.

[3] Gnonlonfoun *et al.* (2022). Inhibition of the growth of *Fusarium tricinctum* and reduction of its enniatin production by *Erwinia gerundensis* isolated from barley kernels. *J. Am. Soc. Brew. Chem*

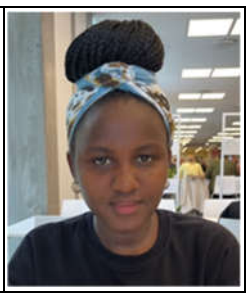
2022

Research subject : Metal-chelating peptides and chromatography: from peptides separation to metals separation

Rachel IRANKUNDA (2nd year)

Laetitia CANABADY-ROCHELLE, Laurence MUHR

Axe BIOPROMO | Axe PERSEVAL



Keywords : Metal-Chelating Peptides (**MCPs**), Immobilized Metal ion Affinity Chromatography (**IMAC**), Surface Plasmon Resonance (**SPR**), chromatography modelling and simulation, separation

General context, scientific issues :

MCPs are obtained from protein hydrolysates and co-products as well and present various applications in nutrition, pharmacy, health, cosmetic and separation processes. Yet, MCPs separation is challenging due to their low concentration in hydrolysates (*i.e.,* complex mixture of peptides). To date, the empirical approach used to discover MCPs consists of many cycles of separation /fractionation followed by biological activity tests until the target peptide identification. This method is time consuming, expensive and finding a target peptide is uncertain.

Objectives and stakes :

Considering the expected SPR-IMAC analogy based on the similar peptide-metal ion interactions, this PhD work aims to simulate the separation of MCPs in IMAC using a transport dispersive model and peptides binding affinity data obtained from SPR.

Methodology :

Peptide sequences to be investigated were obtained from pea proteins theoretical hydrolysis. These synthetic peptides were studied in SPR using a Ni^{2+}-NTA sensor ship to obtain their binding affinity data (K_A, q_{max}) [1], that serve as input data for peptide retention time (**t_R**) simulation, using a transport dispersive model [2] described by the following equation:

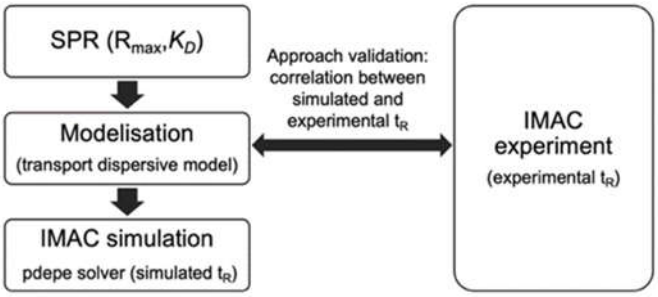
$$\frac{\partial C_i}{\partial t} + \frac{1-\varepsilon_T}{\varepsilon_T}\frac{\partial q_i}{\partial t} + \frac{u}{\varepsilon_T}\frac{\partial C_i}{\partial z} = D_L \frac{\partial^2 C_i}{\partial z^2}$$

$\forall i=1, 2,\ldots,N_c$ and $z \in (0,L)$ given that $\frac{\partial q_i}{\partial t} = k_m(q_i^* - q_i)$ (Linear driving force) and $q_i^* = \frac{q_{max,i} K_{A,i} C_i}{1+\sum_{i=1,n} K_{A,j} C_j}$ (Sorption isotherm equilibrium)

On the other side, the same peptides were investigated in IMAC using a HiFliQ-Ni^{2+}-NTA column in order to make correlation between the experimental t_R and the simulated t_R to validate the approach.

K_D: constant of dissociation; ***K_A:*** Affinity constant; **R_{max}**: maximum response; **C**oncentration of the solute in the mobile phase; **q**: concentration of the solute in the stationary phase; **MW**: molecular weight; **t**: time coordinate; ***z***: axial coordinate; **ε_T**: total porosity; ***u***: the superficial velocity; ***D_L***: apparent axial dispersion coefficient; ***k_m***: lumped mass transfer coefficient; **Nc**: number of components in the system, **L**: column length.

Illustration : Simulation of peptides separation in IMAC



Main results

SPR results show that peptide affinity to Ni^{2+} immobilized on NTA chip depends on peptide amino acid composition and position. Peptides containing histidine and tryptophan show good affinities with some exceptions. On another hand, the peptides with good affinity constant in SPR are also well retained in IMAC (high Tr). Thus, the quantity of imidazole to elute peptides (IMC) increases when the its affinity constant for Ni^{2+} increases. These results validate the analogy between SPR and IMAC.

Besides, the simulation part is under optimisation to validate the approach of simulation of peptides separation in IMAC from SPR data. The proof of concept was validated on small-sized peptides (2-3 residues) [3] and must be extended to peptides with ≃10 residues.

Finally, peptides with good affinities to Ni^{2+} according to SPR have been also investigated to evaluate their ability to inhibit lipid oxidation in oil-in-water emulsions by chelating Fe^{2+} in the frame of an international mobility carried out at Denmark Technical University

References :

[1] Canabady-Rochelle *et al.,* 2018. Food Chem. 239:478–485.
[2] Guiochon *et al.,*2006. Trends Food Sci. Tech. 37 :92–105.
[3] Muhr *et al.,* 2020. J. Sep. Sci. 43 :2031–2041.

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

2022

Research subject : Quantification and impact of microcarriers collisions during mesenchymal stem cell culture in bioreactors to enhance bioproduction process performance

Charlotte Maillot (3rd year)

Eric Olmos, Dominique Toye [1], Natalia de Isla[2]

[1] Laboratory of Chemical Engineering, Université de Liège [2] CNRS, IMoPA, UMR 7365, Vandoeuvre lès-Nancy

Axe BIOPROMO

Keywords : Bioreactor, Mesenchymal Stem Cell culture, Microcarriers

General context, scientific issues :

Mesenchymal stem cell-based therapies require large quantities of cells which have maintained the appropriate quality for therapeutic use. This expansion can be performed using microcarrier-based bioreactor processes for which the biochemical parameters (substrate and/or gas concentration) and mechanical parameters (hydromechanical constraints) can be modified to achieve maximal expansion.

Objectives and stakes :

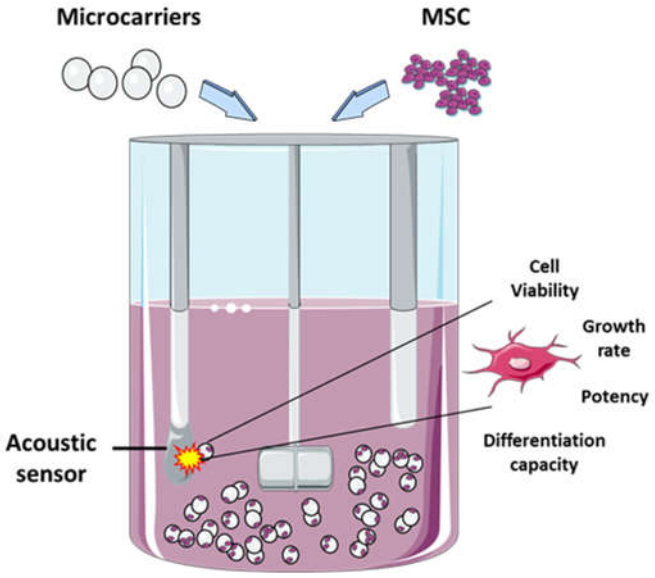
Since mesenchymal stem cells are adherent cells, their expansion can be performed using suspended adhesion supports such as microcarriers (small particles of approximately 200µm in diameter). However, hydromechanical stresses, friction or shocks between microcarriers, are likely to lead to undesired cell death or degradation of cellular quality, resulting in a significant decrease in the productivity of the process. Our objective is to quantify the amount and intensity of collisions between microcarriers and define their impact on the quality of expanded

Methodology :

The impact of collisions on cell growth and the quality of expanded MSC's (clonogenicity, functionality or senescence) will be determined at different scales and using different agitation conditions (Erlenmeyer flasks, spinner flasks and agitated bioreactors). For this, the concentration of suspended particles will be adjusted in different cultures while maintaining similar agitation conditions.

In parallel, the quantification of collisions in an agitated bioreactor and ideally, their intensity, will be performed using acoustic emissions. If successful, these results will be used to define the distribution of these collisions within an agitated bioreactor and correlate with the in-vitro expansion results. Lastly, the analysis of acoustic emission during the progressive suspension and/or settling of microcarriers will be performed in partnership with the university of Liège to correlate with results using light attenuation technique [1] for particle concentration distribution in dynamic conditions.

Illustration : The use of acoustic emission sensors for microcarrier-based MSC cultures



Main results

Cell growth was performed by culturing hMSC's extracted from the Wharton's Jelly of umbilical cords (WJ-MSC's) on Cytodex-1 microcarriers. The concentration of viable microcarriers remained constant, and as a result, the seeding conditions and available surface was maintained. The addition of inert microcarriers, on which cells cannot adhere, was used to increase the number of total particles and thus particle collisions. Analysis of the cells produced will be used to see if the inhibition of cell growth is associated, or not, with a degradation of MSC quality attributes such as clonogenicity, functionality or senescence.

The addition of inert microcarriers has an impact on cell growth which seems to slow down the more inert microcarriers are added. As a result, a compromise between increasing particle concentration (available surface for cell culture) and cell growth may be required. Whether these results are valid in larger scale agitated conditions like bioreactors or spinner flasks remains to be verified.

References :

[1] Delafosse et al. « Solid-Liquid Suspension of Microcarriers in Stirred Tank Bioreactor – Experimental and Numerical Analysis ». Chemical Engineering Science 180 (avril 2018): 52–63. https://doi.org/10.1016/j.ces.2018.01.001.

2022

Research subject : Development and validation of a metabolic model of a hydrogen-producing bacterial consortium

Xavier Marbehan (2nd year)

Stéphane Delaunay and Frantz Fournier

Axe BIOPROMO

Keywords : Metabolic modeling, Flux Balance Analysis (FBA), Biohydrogen, Bacterial interaction

General context, scientific issues :

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

Objectives and stakes :

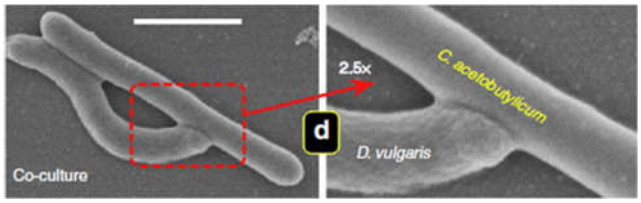
A transfer of metabolites between the two bacterial partners of the consortium is suspected to be responsible for the biohydrogen overproduction. To identify the exchanged metabolites, it is planned to model the global metabolism of the bacterial consortium. This modeling study requires several steps.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

Methodology :

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

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

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



Main results

A simulation of the consortium model with constraints recreating the experimental environment was performed. These constraints were imposed fluxes of glucose consumption by Cac and of a carbon source by Dvu, this one provided exclusively by Cac. The other constraint was the possibility, for both bacteria, to exchange, in the physical bridge (illustration), all their common intracellular metabolites. The fluxes found for the biomass synthesis of each organism and the global hydrogen production were compared with and without exchange between cac and dvu (Fig 1).

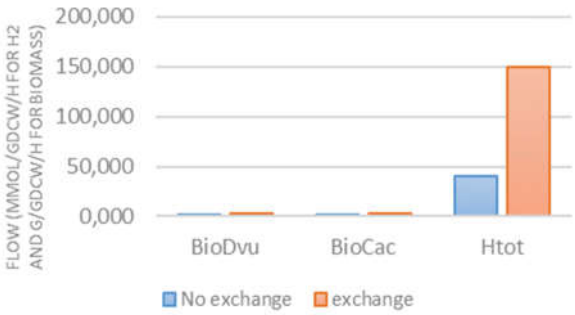


Fig 1. comparison of biomass and hydrogen production fluxes with and without metabolite exchange within the bacterial consortium.

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

References :

[1] Barca et al. « Fermentative Hydrogen Production in an Up-Flow Anaerobic Biofilm Reactor Inoculated with a Co-Culture of Clostridium Acetobutylicum and Desulfovibrio Vulgaris ». Bioresource Technology 221 (décembre 2016): 526 33. https://doi.org/10.1016/j.biortech.2016.09.072.

[2] Xavier Marbehan et al. « Xcom, a multi-objective function for the metabolic modeling of microbial consortia » Poster presented at : BiOPROSCALE; March 28 to 31, 2022; Berlin.

[3] Benomar et al. « Nutritional stress induces exchange of cell material and energetic coupling between bacterial species ». Nature Communication (Feb 2015). DOI: 10.1038/ncomms7283 |www.nature.com/naturecommunications

2022

Research subject : subject: Modelling of hydrodynamics in an agricultural digester

Liliane MEGUE KAMKENG (2nd year)

Éric OLMOS (LRGP) | Benjamin LE-CREURER (Air Liquide)

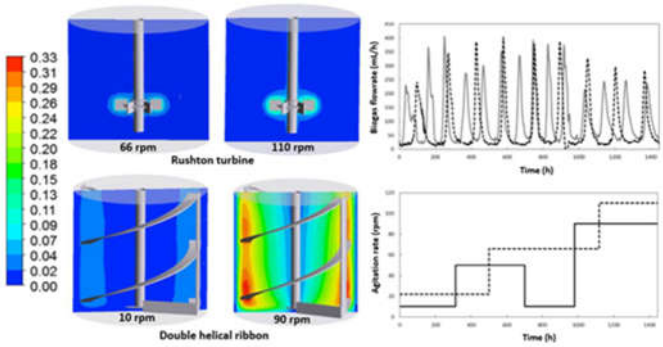
Axe BIOPROMO | Air Liquide

Keywords : Agricultural digester; Scale down; Scale up; Modelling; Hydrodynamics; Rheology

General context, scientific issues :

This thesis is part of the Air Liquide's biogas project which aims to increase the production of biomethane and to reduce the production costs. Industrial digesters are usually equipped with an agitation system whose main functions are to: ensure a good homogeneity (such as substrate and temperature), release the generated biogas, avoid sedimentation etc. However, the energy consumption of the agitators must also be considered because it represents most of the operational expenditures (OPEX). Applying an optimal agitation (sufficient but not excessive) would not only improve the production of biomethane but also limit the process energy cost

Illustration : Effect of shear stress and impeller design on biogas production in anaerobic digesters [1]

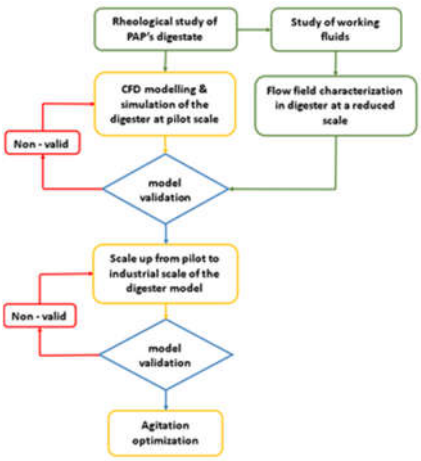


Objectives and stakes :

This thesis aims to describe the hydrodynamics of an industrial agricultural digester. More specifically this research intends to optimize the agitation of the industrial digester from Pot au Pin Energie (PAP) in Cestas - France so as to limit the energy consumption and avoid sedimentation. The PAP's digester is a continuous stirred tank reactor (CSTR) of roughly 2000 m^3 volume and fed with a mixture of corn silage and rye

Methodology :

First, experimental work will be carried out to characterize PAP's digestate rheology and flow field in digester at a reduced scale. Then the CFD modelling and simulation of the digester at pilot scale will be performed followed by model validation. Finally, scale up from pilot to industrial scale of the digester to predict hydrodynamics in PAP digester.



Main results

1. Rheology of digestate

- PAP's digestate has a non-Newtonian shear-thinning with a yield stress behavior described by the power law and the Herschel Bulkley model.

- Models linking solid matter and rheological parameters has been established.

- A coarse grinding has no significant impact on the rheology of the digestate, while a fine grinding result in decreases in viscosity and yield stress.

2. CFD Modeling

- CFD simulations of the PAP digester were performed. The total power required by the agitators obtained from CFD and the electrical power measured on the production site are close. The cavern (well-mixed zone) diameter obtained from CFD is similar to the value calculated with a model from the literature [2].

References :

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[2] Solomon, J., Elson, T.P., Nienow, A.W., Pace, G.W., 1981. Chemical Engineering Communications 11, 143–164.

2022

Research subject : Synthesis of photosensitizers to target, detect and destroy peritoneal carcinomatosis while activating the immune system.

Morgane Moinard (1st year)

Céline Frochot, Nadira Delhem (OncoThai, Lille)

Axe BIOPROMO

Keywords : photodynamic therapy, photosensitizers, folic acid, ovarian cancer, peritoneal carcinomatosis

General context, scientific issues :

Because of a lack of symptoms, ovarian cancer is often diagnosed at an advanced stage of the disease. Despite a conventional treatment combining platinum-based chemotherapy to maximal cytoreduction surgery, about 60% of women relapse[1]. This high recurrence rate is mainly due to the presence of microscopic peritoneal carcinomatosis residues, not visible to the naked eye of the surgeon, which were not removed after surgery. In order to increase the life expectancy of diseased women, our research project aimed to specifically target this microscopic tumoral residues.

Our main strategy is the active targeting of the α isoform of folic acid receptor (FRα), by using photodynamic therapy (PDT). In fact, this receptor is overexpressed by various cancer cells, including those of ovarian origin[2]. Furthermore, the main advantage by targeting FRα is that this latter is only slightly expressed by healthy cells and tissues, allowing a specific target to ovarian cancer cells. In this context, various photosensitizers (PS) coupled to folic acid molecule has been previously synthetized by our research group. One of them was the object of one patent. But some stability issues were observed with the folic acid molecule[3]. In fact, some degradation products were observed upon illumination. Therefore, our main objective is to find folic acid analogue which could circumvent this stability problem. Indeed, based on molecular docking studies, some folic acid analogues with a potential affinity to folic acid receptor should be developed

Objectives and stakes :

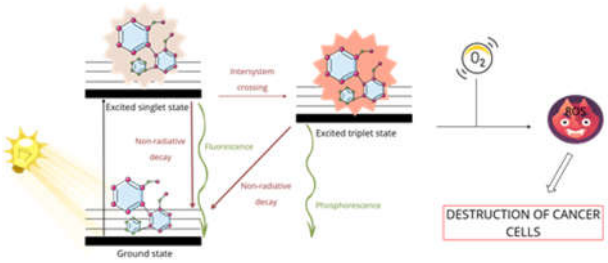
Our goal is to synthetize these new folic acid analogues which would potentially target the FRα receptor and to combine them via a PEG spacer with a PS, for PDT treatment of peritoneal carcinomatosis. Three main parts composed our project:

- Synthesis of folic acid analogues followed by coupling with a PS.
- Investigation of photophysical properties of the newly synthetized PS.

Methodology :

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

Illustration : Photodynamic therapy principle.



Main results

Proof of concept:

To established the proof of concept, we have thought coupling folic acid analogues to a PS via a PEG spacer, to obtain a targeted PDT effect towards ovarian cancer cells.

- **Synthesis, purification and characterization** of a first new photosensitizer (PSAAF), resulting from a coupling between a folic acid analogue and pyropheophorbide *a* via a PEG spacer.
- **Photophysical properties** (quantum yields and lifetimes of fluorescence and singlet oxygen) of PSAAF was investigated in EtOH. It demonstrated a quantum yield of fluorescence of 0.26 and a singlet oxygen quantum yield of 0.41.
- **No dark toxicity** was observed *in vitro* for a concentration up to 9 µM.
- **Phototoxicity** in three cancer cell lines (the SKOV3, OVCAR3 and HT1080). In each cancer cell lines, after illumination with a 672 nm laser for 5 minutes, cellular viability was closed to 0% at concentration of 1.8 µM and 4.5 µM. 100% of cells were killed at a concentration of 9 µM.

Stability studies

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

Synthesis of further folic acid analogues

We will also synthesize a second folic acid analogue, discovered during the molecular docking studies. This second analogue will also be coupled to various PS via PEG spacer.

References :

1 T. Al Rawahi, A. D. Lopes, R. E. Bristow, A. Bryant, A. Elattar, S. Chattopadhyay and K. Galaal, *Cochrane Database of Systematic Reviews*,, DOI:10.1002/14651858.CD008765.pub3.

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4 M. Moinard, J. Augustin, M. Carrier, E. Da Maïa, A. Penel, J. Belghiti, M. Nikpayam, C. Gonthier, G. Canlorbe, S. Acherar, N. Delhem, C. Frochot, C.Uzan, H. Azaïs, *Pharmaceuticals*, 2022, just submitted

2022

Research subject : Application and optimization of extraction of bioactive compounds from a medicinal plant *Rhamnus alaternus* and evaluation of its chemical potential and its phytopharmaceutical properties

Amine NEKKAA (4th year)

Laetitia CANABADY-ROCHELLE, Akila BENAISSA

Axe BIOPROMO

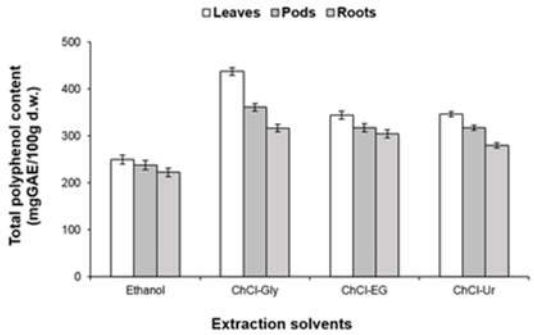
Keywords : *Rhamnus alaternus*, extraction processes, natural deep eutectic solvents, green extraction, polyphenols, antioxidant activity, antibacterial activity.

General context, scientific issues :

Recently, the green extraction techniques have become of utmost importance in research related to biomolecules production. Therefore, food, cosmetic and pharmaceutical industries operated a transition from conventional extraction to the green extraction processes, using alternative cost-effective and earth-friendly solvents[1].

Rhamnus alaternus is empirically considered as a medicinal plant. Hence, this source of natural compounds possesses pharmacological activities, and is traditionally used for its curative effects to treat some symptoms and diseases[2]

Illustration : Total phenolic content (TPC) of *R. alaternus's* leaves, pods and roots extracted with natural deep eutectic solvents (NaDESs): ChCl-Gly, ChCl-EG, ChCl-Ur and Ethanol as reference[3]



Objectives and stakes :

The aim of this PhD was to evaluate the efficiency of three Natural Deep Eutectic Solvents (**NaDESs**), in order to develop green and sustainable process for the extraction of high-value phenolic compounds, from various parts of *R. alaternus* and to investigate the bioactive properties of collected extracts.

Methodology :

Three choline chloride-based NaDESs (*i.e.,* choline chloride-glycerol: **ChCl-Gly**; choline chloride-ethylene glycol: **ChCl-EG** and choline chloride-urea: **ChCl-Ur** with molar ratio of (1:2)) in addition to the ethanol as reference solvent were used for efficient extraction of total phenolic compounds (**TPC**) from the leaves, pods and roots of *Rhamnus alaternus* plant. In each extract, their total phenolic content using Folin Ciocalteu test and their antioxidant activity were evaluated (*i.e.,* free radical scavenging, reducing power and iron chelating capacity). More, their antibacterial activity was carried out against Gram-positive and Gram-negative strains including *Staphylococcus aureus, Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Klebsiella pneumoniae*[3]. The minimum inhibitory concentrations (**MIC**) were determined using the microdilution broth method in 96-well microplates. The best extract in term of biological activities obtained from the three parts of *R. alaternus* was characterized and quantified by mass spectrometry (HPLC-MS/MS) to determine their bioactive compounds.

Main results

The investigated extracts presented antioxidant and antimicrobial activities. The leaves extracts obtained by the choline chloride-glycerol (ChCl-Gly) mixture exhibited a high value of TPC (437.7 – 317.0 mg GAE/100 g d.w.) with the best antioxidant properties. The study of various extracts indicated that ChCl-Gly is a sustainable NaDES and alternative solvent with the highest extraction efficiency.
HPLC-MS/MS analysis confirmed that the phenolic acids and flavonoids were the main antioxidant compounds present in the extracts.

References :

[1] Nekkaa, A; *et al.* (2021). Optimization of the extraction process of bioactive compounds from *Rhamnus alaternus* leaves using Box-Behnken experimental design. *JARMAP.* doi.org/10.1016/j.jarmap.2021.100345.

[2] Nekkaa, A; *et al. (2021). Rhamnus alaternus plant:* extraction of bioactive fractions and evaluation of their pharmacological and phytochemical properties. *Antioxidants, 10,1–21. doi.org/10.3390/antiox10020300.*

[3] Nekkaa, A; *et al. (2022).* Green and Innovative Extraction of Polyphenols from *Rhamnus alaternus* using Natural Deep Eutectic Solvents and evaluation of their bioactivities. *ACS Sustainable Chemistry & Engineering, In progress.*

Acknowledgements

This research work supported by PHC-Tassili (Code 20MDU917) was labelized by the "Impact Biomolecules" project of the "Lorraine Université d'Excellence" (Investissements d'avenir – ANR project number 15-004)

2022

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

Adèle SCHINI 1st year)

Emmanuel GUEDON, Bruno EBEL

Axe BIOPROMO

Keywords : bioprocesses, spectroscopies, *in situ* sensors, animal cell culture, CHO, bioreactor, optimization

General context, scientific issues :

The PAT (Process Analytical Technology) approach consists in developing on-line monitoring methodologies for production processes to ensure their real-time control. However, apart from the classical probes (pH, temperature, O_2 concentration), the bioreactors of animal cell cultures remain very little instrumented. To overcome this lack, spectroscopic tools coupled to sterilizable fiber optic probes are beginning to be evaluated.

Objectives and stakes :

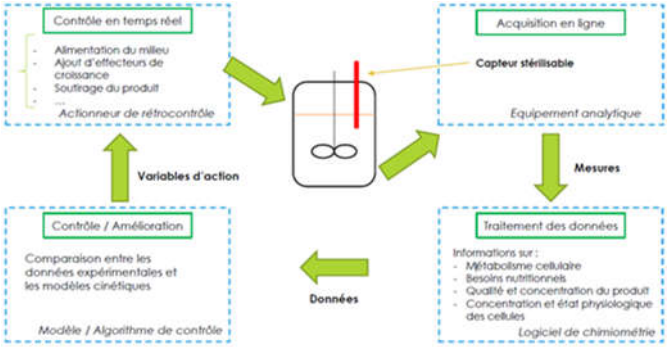
The overall objective of this thesis work is to lay the first building blocks for the combination of sensors used in bioprocesses. Thus, the monitoring of industrial processes could move from "Process Control" to "Quality Attribute" which gives access to qualitative and quantitative information on the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

Methodology :

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

Several cell culture runs will be performed to assess the accuracy of the modeling approaches.

Illustration : PAT approach for bioreactors automation



Main results

The final modeling will give the user access to qualitative and quantitative information about the current cell culture

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 multiple variables toward real-time monitoring of CHO cell bioreactor cultures. Biochemical Engineering Journal, 137, 205-213.

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2022

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

Bastien THAUVIN (1st year)

Latifa CHEBIL, Eric Olmos

Axe BIOPROMO

Keywords : culture, microcarrier, bead-to-bead transfer, mesenchymal stem cells, bioreactor

General context, scientific issues :

Extracellular vesicles (EVs) produced by mesenchymal stem cells (MSC) have regenerative properties and are promising as cell-free therapy to repair damaged tissues. 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 but a large number of cells is still required. MSC are anchorage dependant and need specific surface area for their expansion. Conventional 2-Dimensional systems are time consuming and allows insufficient control of cell culture parameters. Development of 3D culture systems with microcarriers tend to give interesting solutions to these issues. Nevertheless, even with these systems, high cell density could lead to cell growth inhibition by confluence and aggregates apparition which are harmful for EVs production performances

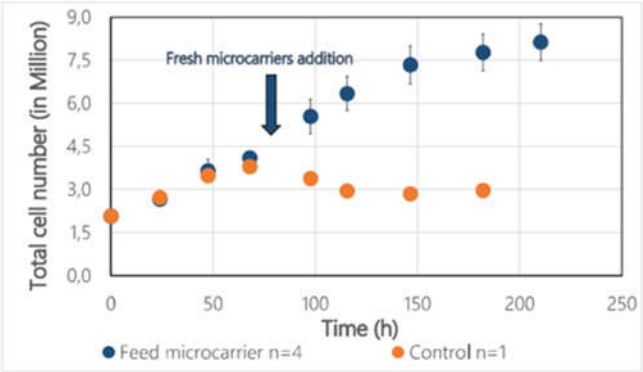
Objectives and stakes :

MSC are able de migrate from confluent microcarrier to new one. This phenomenon is called bead-to-bead transfer. Adding fresh microcarriers increase surface area available for cell growth to avoid confluent. This could permit to control cell density on microcarriers and scale-up without using enzyme for cell detachment. The aim of this PhD project is to design a cell culture process compatible with reglementary requirements and based on bead-to-bead transfer as scale-up method to produce large amount of human adipose derived stem cells (ADSCh) to support EVs therapies development.

Methodology :

ADSCh are cultivated in 2D systems before being inoculated on microcarriers in spinner flasks with human platelet supplemented media. Samples are taken daily to monitor metabolites (glucose, lactate & LDH) with a an automate Gallery and to check cell distribution on microcarrier by nuclei staining with DAPI and images analysis from epifluorescence microscope. New microcarriers are added according to cells per microcarrier ratio and glucose consumption rate. After each feed, 24 hours of intermittent agitation is applied to promote cell migration

Illustration : Effect of fresh microcarriers addition on ADSCh culture on microcarrier in 100 mL spinner flasks



Main results

Microcarriers addition increase final harvest and allow to maintain cell culture during longer period than the control. It also permits to reduce number of overpopulated microcarriers (>12 cells per bead). This technique allows to limit the inhibition caused by confluence and delay aggregate apparition. Moreover 24 h of intermittent is efficient to favour cell migration on new beads with 97,5 % of microcarriers occupied by at least one cell. Nevertheless, timing of addition is a critical parameter which need to be optimized to allow best culture performances. Bead to bead is promising to obtain large number of cells required for the development EVs based therapies. However, process parameters have to be defined to maintain high expansion rate. Finally, it could be considered to automate microcarriers addition with on-line solutions like permittivity measurement to have more control on process and ensure low variation between batchs.

References :

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2022

Research subject : Electromicrobial enhancement of biohydrogen production from organic wastes

Delphine Truong (3rd year)

Emmanuel Guedon (LRGP) & Mathieu Etienne (LCPME)

Axe BIOPROMO

Keywords : Biohydrogen production, dark fermentation, Microbial electrolysis cell, tubular membrane, bioelectrochemical system, organic wastes

General context, scientific issues :

In the context of the energy crisis which depends on fossil fuels, research tries to develop method for green energy production such as hydrogen. Hydrogen is commonly used as raw material in many fields but it could be also used as a powerful clean energy vector [1]. Different methods already exist to produce H_2, but they are associated to CO_2 and the process needs a huge amount of external energy (even for the water electrolyse which is the only green method used nowadays)[2]. Bioproduction of hydrogen is an alternative and is intensively studied, mainly for concept, process accessibility and cost. One of these methods is the use of dark fermentation (DF) to produce H_2 from organic wastes by anaerobic microorganisms but it permits to produce only 2.4 mol_{H2}/mol_{hexose} instead of 4 mol_{h2}/mol_{hexose}[3]. This is probably due to methanogenic bacteria that decrease the H_2 production. However, effluents from dark fermentation can be oxidised to increase the production yield. Our studies explore the possibility to combine Microbial Electrolysis Cells (MEC) and DF to produce more H_2. In fact, MEC can oxidise fermentation co-products (mainly acids) to create a current that allow the reduction of protons in a bioelectrode. However, both methods need an external energy for the non-spontaneous reaction of the acids oxidation that cannot be overcome by the current produced. Thus, many studies separated MEC and DF by transferring effluents from fermentation phase into a double chamber MEC which increase the complexity of the process in terms of conception, materials and maintenance.

Objectives and stakes :

The aim of the work is to integrate DF and MEC into the same bioreactor to produce H_2 without external energy supply, using at first pure cultures of *Clostridium sp.*, and constituted microbial ecosystem taken from a biomethanizer (experimental farm, la Bouzule, université de Lorraine). The objectives are the production of current and a microbial specialisation at both electrodes, in order to improve H_2 production

Methodology :

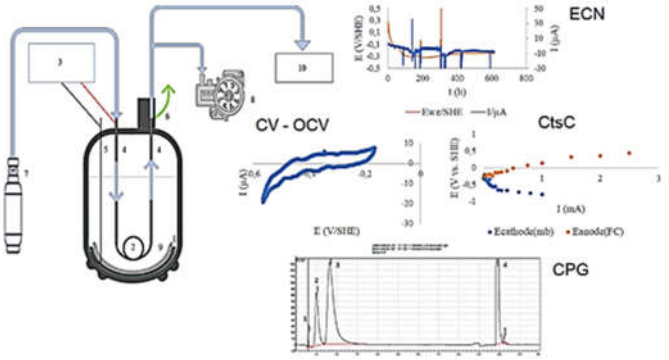
Electrodes

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

Culture in bioreactor

A 5 L scale bioreactor, is used as the only chamber of reactions. Organic matter is taken from a biomethanizer and used with or without treatment (to inhibit methanogenic bacteria). The pH mean of each culture is 7.5 ± 0,2 with a conductivity of 13 ± 2 mS/cm and an ohmic drop of the media was 14,6 Ω. The gas produced were analysed using a gas chromatography

Illustration : Experimental approach



Main results

Electrochemical Noise (ECN)

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

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

Open Circuit Potential (OCP) and Circuit Voltage (CV)

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

The O_2 contamination was controlled and methanogens microorganism were inhibited. H_2 production was observed in gas chromatography which means that its production could be reach at the system potential.

Constant Current (CstC)

To determine the limit of the system, a range of current was applied on

References :

[1] Association Française pour l'hydrogène et les piles à combustibles (AFHYPAC), 2016. Production et consommation d'hydrogène aujourd'hui.

[2] Ministère de la transition écologique et solidaire. 2018. Plan de déploiement de l'hydrogène pour la transition énergétique.

[3] Pierra M., 2013. Couplage de la fermentation sombre et de l'électrolyse microbienne pour la production d'hydrogène : formation et maintenance du biofilm électro-actif

2022

Research subject : Study of the impact of enzymatic acylation of amino acids on the rheology of acylated derivatives products

Ahmed ZOUARI

Isabelle CHEVALOT

Axe BIOPROMO

Keywords : Emulsion, Amino-acids, Fatty acids, Enzymatic acylation, Acyl-amino acids, Rheological properties, Food, Response surface methodology

General context, scientific issues :

Emulsion stability in food industries has been considered as an important key factor in food preparation and sensory properties evaluation. Some of the used emulsifier in food industries are almost chemically synthetized and may have low stability during manufacturing and storage. This concern could affect the rheological properties during food manufacturing due to the emulsion instability. That's why new emulsifiers, such as Acyl-amino acids, should be produced and studied.

Objectives and stakes :

In this project, the evolution of the structure of amino-acylated products will be studied using an approach based on the change of their rheological behavior. Indeed, acylated amino acids are enzymatically produced and present very interesting techno-functional properties as bio-based surfactants. The acylation reaction occurs between a fatty acid and an amino acid. The choice of the chain length of the fatty acid and the nature of the amino acid as well as the concentration of the Acyl-amino acids in the formulated product will have an impact on their surface active properties and subsequently on the rheology of the formulated products.

Methodology :

First of all, a concise review of the state of the art during the two decades is being realized. This step will indicate the recent scientific findings related to use of Acyl-amino acids as bio-surfactant in serval applications. Then, based on response surface methodology and experimental design approach a preliminary study using different biosynthesized Acyl-amino acids will be applied to prepare a simple food matrix (water/Oil/emulsifier). The emulsion microstructure, the droplet sizes, the emulsifying activity index (EAI) and emulsion stability index (ESI) as well as the viscosity of the preparation will be studied. Based on these results some other complex food structure such as dairy products will be studied.

Illustration : Graphical abstract

Main results

State of the art analysis indicated that bio-emulsifiers were used in several applications such as controlling and preventing biofilm formation on food surfaces [1] and food industries equipment (anti-biofilm agent) [2]. Biosurfactants were also used as antibacterial agent since they can change the permeability of the plasma membrane of bacterial cells [3]. In addition, it was shown that bio-surfactants acted as active food ingredient since they presented interesting emulsifying proprieties and great capacity to reduce the surface tension. Indeed, it was found that the use of Rhamnolipids (Bio-surfactant) enhanced the stability of butter cream and non-dairy cream (composed of vegetable oil) [4]. Besides, Zouari et al., (2016), proved that lipopeptide addition while preparing dough improved the quality of wheat sesame cookies [5].

From the literature review it was evident that biosurfactant contribute to the stability of food formulation and therefore the consistency and texture of the food products through the modification of the rheological properties of food products

References :

[1] Campos, J. M., Montenegro Stamford, T. L., Sarubbo, L. A., de Luna, J. M., Rufino, R. D., & Banat, I. M. (2013). Microbial biosurfactants as additives for food industries. Biotechnology progress, 29(5), 1097-1108.

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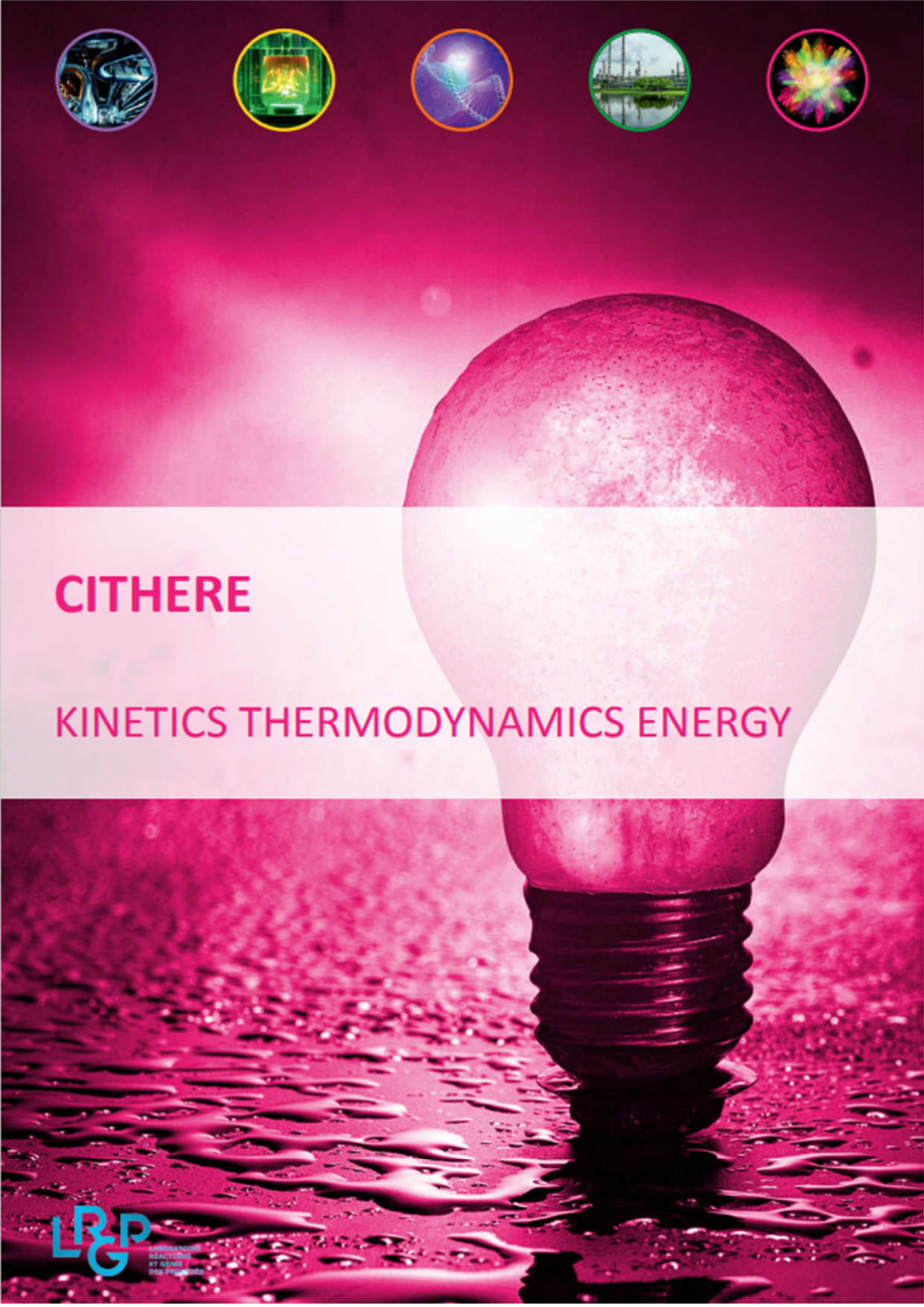


CITHERE

KINETICS THERMODYNAMICS ENERGY

LRGP

2022

Research subject : Valorization of Olive pomace through fast oxidative pyrolysis

Mohamed Aissaoui (Research Engineer)

Guillain Mauviel, Yann Le Brech

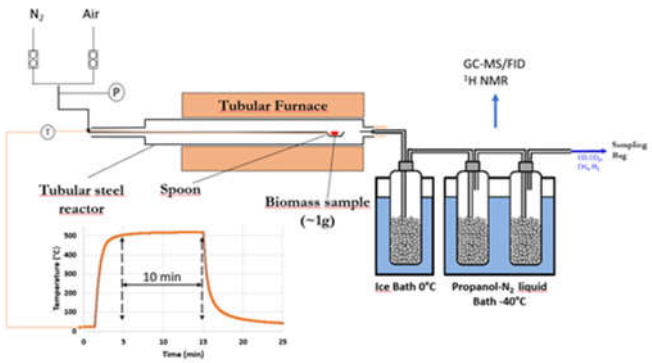
Axe CITHERE

Keywords : Biomass, Fast pyrolysis, oxidative pyrolysis, tubular reactor

General context, scientific issues :

The management of Olive Pomace creates major environmental difficulties, and finding a sustainable way to manage them is an important requirement[1]. The thermochemical conversion of OP residues allows recovering value-added products which can be used in several fields. One of the main thermochemical valorizations is pyrolysis.

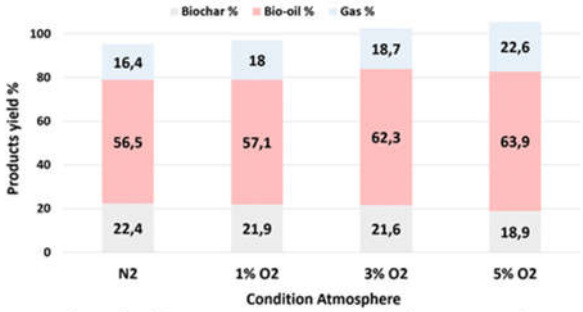
Illustration : **Tubular reactor diagram**



Objectives and stakes :

This study assesses the oxidative fast pyrolysis feasibility to convert the OP into biofuels (bio-oil and syngas) and biochar which can be used as fertilizer or adsorbent. The potential advantage of oxidative pyrolysis is to allow the industrial reactors to be autothermal (no external heat), whereas complex allothermal reactors are needed in the case of classical pyrolysis with inert gas[2]. The goal of this study is to determine the influence of the O_2 content on the product yields and composition.

Main results



Mass Balance for Olive Pomace Fast pyrolysis at different Atmosphere

The oxidative pyrolysis increased the yield of bio-oil and gas quantified by micro-GC (specially CO_2) and slightly decreased the yield of biochar.
The oxidative pyrolysis maintains a comparable quality of bio-oil with aromatic and acids.
The composition of biochar is affected by the atmosphere condition but is still rich in carbon.

This study confirms the feasibility of scaling-up the autothermal pyrolysis to convert the OP into biofuels (bio-oil and syngas) and biochar which can be used as fertilizer or adsorbent

Methodology :

The OP was fast pyrolyzed using a spoon oven (tubular furnace) at 500°C with 2.5s gas residence time inside the reactor. The solid holding time is set 10 minutes at 500°C. Different atmospheres were used: totally inert (100% N_2) or oxidative (mixture of nitrogen (N_2) and air with different ratios to obtain 1, 3 or 5% of O_2 at the inlet). The recovered biochar was characterized by Ultimate analysis, FTIR and $_{13}$C NMR CP MAS. The condensed bio-oil was characterized using GC-MS-FID and $_1$H NMR and the gas produced was analyzed using a Micro GC

References :

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2022

Research subject : Reactive Working Fluids for Heat Pumps and Power Cycles

Aya BARAKAT

Jean-Noël JAUBERT, Silvia LASALA

Axe CITHERE

Keywords : Reactive fluids, thermodynamic cycles, thermodynamic analysis, chemical equilibrium, experimental validation, reaction design

General context, scientific issues :

- At present, the thermal engine remains the most reliable commercialized technology enabling the conversion of thermal energy into electricity. Although classical thermal engines are particularly suitable for high-temperature and high-power fossil fueled thermal sources, their employment to convert the lower-grade energy content of renewable and waste heat sources reveals strong performance limitations. Therefore, this thesis intends to contribute to the development of a highly efficient and extremely compact closed power cycle owing its promising–and still unexploited–performances to the **use of a properly selected equilibrated reactive working fluid, instead of a classical inert one**. Preliminary calculations[1] have indeed shown that the simultaneous conversion of the thermal and chemical energy of reactive fluids may result in the intensification of closed power cycles.
- Fossil-fuel based heating systems are still heavily used in the context of space, water, and industrial processes heating. However, in order to meet the net zero emissions by 2050 scenario, greener and more efficient heating technologies like heat pumps are needed. Hence, this thesis investigates the potential of reactive fluids in a heat pump system.

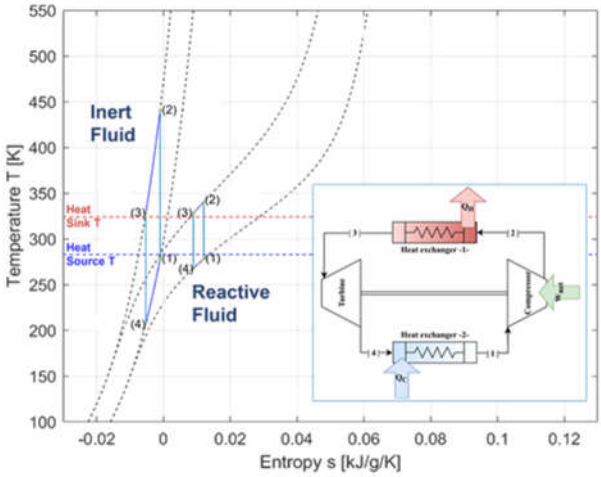
Objectives and stakes :

The objective of this thesis is, firstly, to assess the use of a fictive reactive fluids in power cycles and heat pump systems for different operating conditions and reaction stoichiometries, secondly, develop an original methodology enabling the selection of existing suitable reactive fluids for different operating conditions, and then develop a test rig enabling the validation of the theoretical calculations performed in the first part of the

Methodology :

The approach of selecting optimal working fluids that will be followed is twofold. The research of the reactive fluid will be performed, on one hand, considering reactions whose thermodynamic and kinetic data are present in available databases and, on the other hand, considering designed reactions with specific enthalpy, entropy of reaction, and kinetics. The experimental apparatus will consist of a micro-power cycle initially tested with pure gaseous CO2 and, as a second step, with a preliminary selected reactive fluid. Experimental measurements of the reactive fluid composition throughout the cycle will be performed using online Raman spectroscopy measurements

Illustration : T-s diagram of an inert fluid vs. reactive fluid in a heat pump system



Main results

For power systems, preliminary calculations show that the use of specific reactive fluids (i.e., characterized by specific stoichiometric and thermal properties) enables the simultaneous maximization of the work generated by expansion and minimization of the work required for compression, resulting in an extremely high net work output. It is also observed that properly selected reactive fluids allow obtaining the best performances at extremely low and cost-effective pressure ratios.
Furthermore, the net power obtained by a Brayton cycle working with reactive fluids is increased by more than 140% with respect to that of the most-efficient comparable inert fluid. Preliminary results also show that the higher is the increase in power output, the lower is the increase in efficiency. Nonetheless, a range of potential efficient working fluids for power cycles that provide a desirable increase in both power output and efficiency is anticipated.
Applying the same methodology to heat pumps, results show an increase in the coefficient of performance (COP) of a system utilizing reactive fluids that can reach 212% compared to an inert fluid system. However, there exists a trade-off between the system's COP and the required mass flow rate that dictates the turbomachinery design.

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 Convers. Manag., vol. 229, p. 113685, Feb. 2021, doi: 10.1016/j.enconman.2020.113685

2022	**Research subject : Pyrolysis of invasive plants for the production of biochar and bio-oil: the case of Japanese knotweed**	

Manon BECHIKHI (Engineer)

Anthony DUFOUR

Axe CITHERE

Keywords : Invasive plant, Pyrolysis, Biochar, Bio-oil

General context, scientific issues :

Japanese knotweed (JKW) is an invasive plant responsible for the fragility of our environment and infrastructure[1]. This invasive plant is present in many countries worldwide[2], where it causes many damages. Its proliferation is exponentially: a simple fragment of rhizome (~10cm) allows to regenerate a new plant[3].

Thus, JKW can generate up to 30 tons of dry matter per hectare[4]. But, at this moment, no method has proven to be effective to eliminate it.

Consequently, its deposits are significant. So, its use as a source of energy might be an answer to problems of treatment of green waste.

Methodology :

For this study, JKW was collected from two sites in the Metropolitan Metz. It is divided into three parts: rhizome, stem and leaf. These biomasses have been subjected to fast pyrolysis at 773K in a fixed-bed reactor under an inert atmosphere (continuous nitrogen flow). Bio-oils were collected by condensation, char were recovered in a quartz reactor. At the exit of the system, gases formed during the pyrolysis experiments were collected with a tedlar bag.

The fast pyrolysis products (bio-oils, biochar, and non-condensable gas) have been characterized by physical and physicochemical techniques (GC/MS, FT ICR MS, XRF, SEM, EDX, µGC…).

Objectives and stakes :

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

Main results

JKW pyrolysis generates approximately 15, 30 and 55% of gases, biochar and bio-oil respectively. The characterization of different fast pyrolysis products highlights the bio-oils richness in compounds of interest (hydrocarbon, alcohols, …). Also, the composition of biochar focus their use for soil amendment or active carbon. This process of pyrolysis formed different gases: CO_2, CO, CH_4 and H_2. Finally, aluminum is observed at the rhizome surface (biomass and char).

References :

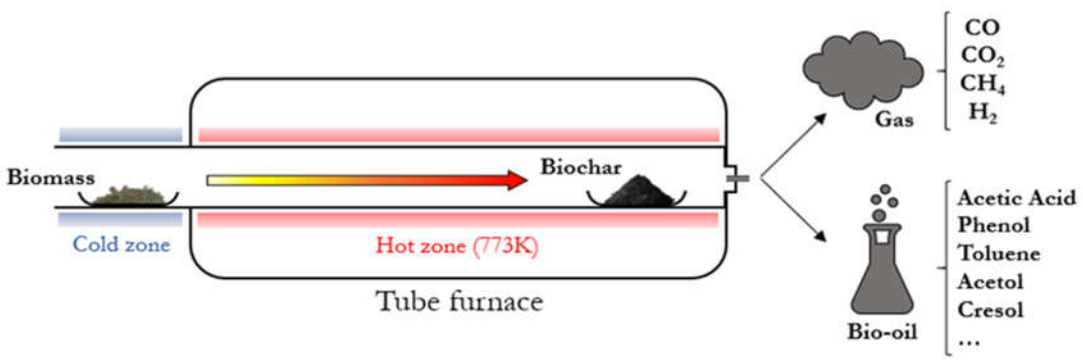
[1] Navratil, O. et al. Distribution of Asian knotweeds on the Rhône River basin, France: A multi-scale model of invasibility that combines biophysical and anthropogenic factors, *Science of the Total Environment*, **2021**, 142995

[2] Beerling, D.J. et al. Fallopia Japonica (Houtt.) Ronse Decraene, *Journal of Ecology*, **1994**, 959-979

[3] Bailey, J.P. et al. Asexual Spread versus Sexual Reproduction and Evolution in Japanese Knotweed, *Biol Invasions*, **2009**, 1189-1203

[4] Schnitzler, A. et al. La renouée du Japon, une dangereuse conquête de l'Ouest, *La recherche*, n°365, **2003**, 50-54

Illustration :



2022

Research subject : Experimental study of the impact of biofuels on the oxidation stability and combustion pollutants of fuels

Ryma BENRABAH (1st year)

Baptiste SIRJEAN, Pierre-Alexandre GLAUDE

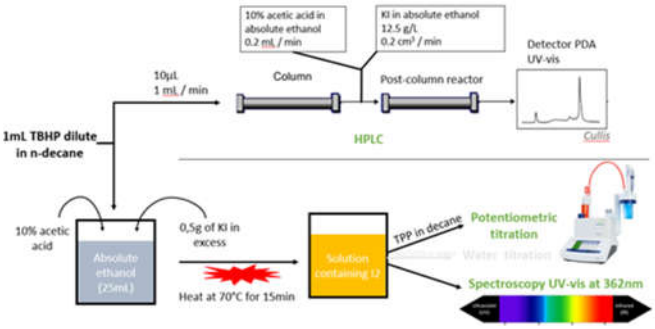
Axe CITHERE

Keywords : (Bio)fuel aging, Liquid phase oxidation, microchannel, kinetic study, HPLC

General context, scientific issues :

Nowadays the increase of the share of biofuels in the transport sector, imposed by European regulations, requires studying their impacts on the liquid phase aging of conventional fuels in tanks. The thermal oxidation of liquid fuels stability of fuels is a key factor in the transportation and the energy fields and induces structural changes in the fuels, leading to safety problems and engine malfunction [1]. This stability can be jeopardized by the slow oxidation of fuels occurring during their storage, manipulation, and use in engines [2].

Illustration :



Objectives and stakes :

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

Methodology :

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

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

The methodology is detailed in the illustration part.

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

Main results

The quantification of peroxide by iodometric titration, in organic solution, shows that it is more reproducible and has a detection range more interesting for our purpose

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

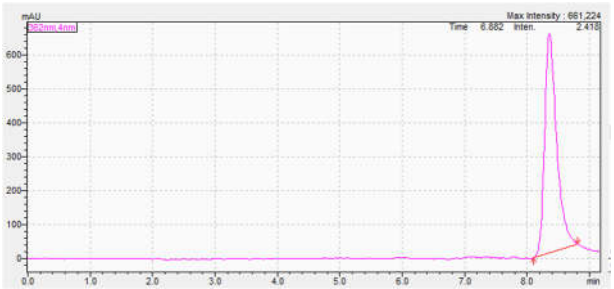


Figure 1: Chromatogram of TBHP diluted in isooctane 10^4 times detected at 362nm.

By comparing each method, we were able to determine the detection range of each technique.

No results yet on the microchannel reactor.

References :

[1] West ZJ. Studies of Jet Fuel Autoxidation Chemistry: Catalytic Hydroperoxide Decomposition & High Heat Flux Effects. *Univ Dayt*. 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

2022

Research subject : Ligno-cellulosic biomass catalytic liquefaction for phenolic compounds production

Pierre-Alann CABLÉ (3rd year)

Fabrice MUTELET, Yann LE BRECH

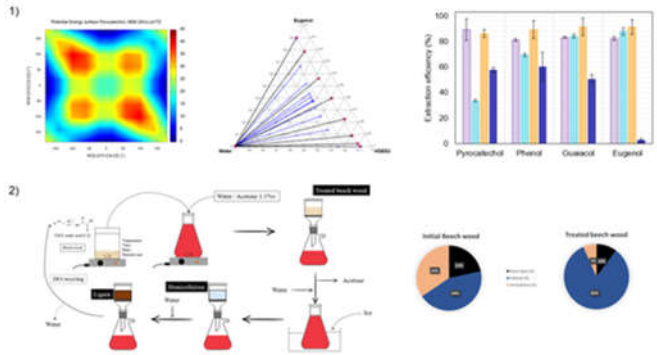
Axe CITHERE

Keywords : Biomass, Deep eutectic solvent, Liquefaction, Thermodynamic, liquid-liquid extraction, computational chemistry, COSMO-RS, Phenolic compounds, Liquid-liquid equilibria

General context, scientific issues :

Green chemistry promotes the use of renewable resources and eco-friendly processes. Lignocellulosic biomass (LCB) is the main renewable carbon source on earth. LCB can be used to substitute petroleum resources for the production of phenolic compounds (PCs) (high-added value molecules) by using thermochemical processes (i.e. liquefaction). Nevertheless, the separation of PCs is complex and remains an issue (distillation, liquid-liquid extraction with organic solvent). Moreover, biomass solubilisation recalcitrance is also an issue for the development of "biorefinery". Therefore, several pre-treatment processes can be involved but the environmental impact is not negligible.

Illustration : Scientific strategies to answer the two problematics Scientific strategies to answer the two problematics



Objectives and stakes :

This work investigates the use of new type of solvents (deep eutectic solvents: DESs) in the field of biomass valorisation. In a first part, hydrophobic DESs (HDESs) are used for the extraction of phenolic compounds from aqueous media and from liquefaction bio-oil (1). In a second part, hydrophilic DESs are used for LCB pre-treatment in order to isolate lignin, hemicellulose and cellulose (2).

Methodology :

1) A theoretical study based on quantum chemistry (COSMO-RS, *ab initio*) is used to determine the most efficient extraction solvents and to investigate the interactions between DES and PCs (H bonding).
Then, liquid-liquid equilibria of ternary systems {HDES-Water -PCs} are determined to evaluate the potential to use the selected HDESs as an extractant media.
Efficiency of selected solvents are evaluated on PCs extraction from synthetic oil and from liquefaction bio-oil. Liquefaction are performed in a high-pressure reactor with water in alkaline conditions on beech wood.

2) A box-Behnken design is used for the optimisation of beech wood delignification (lignin extraction). Several analyses (TGA, NMR, FTIR, CHNS…) have been made on solid fractions (lignin – hemicellulose and cellulose) in order to evaluate the pre-treatment impact.

Main results

1) Phenolic compounds have stronger interaction with HDES than with water according to the results of quantum chemistry calculations. These results are confirmed with the thermodynamic study but performance of the selected HDESs appears to be similar. Extraction of PCs from synthetic oil allows a more effective comparison and the HDES octanoic acid-menthol [2:1] have the highest extraction efficiency. Extraction on liquefaction-bio-oil shows that the selected HDES is able to extract some polyphenols molecules but not monomers.
2) The Box-Behnken design gives the following optimised parameters for the delignification process: 65°C – 22h – 2% w. Based on the initial wood mass, a delignification efficiency of 54% is reported. Moreover, the treated wood is composed of 83% of cellulose (44% initially). During the process,

References :

[1] Van Osch et al., Hydrophobic deep eutectic solvents as water-immiscible extractants. *Green Chem.* **2015**, 4518-4521
[2] McCann et Carpita, Biomass recalcitrance: a multi-scale, multi-factor, and conversion-specific property. *Journal of Experimental botany.* **2015**, 4109-4118
[3] Schutyser et al., Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerization and upgrading. *Chemical Society Reviews* **2018**, 852-908

2022

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

Fabiola CITRANGOLO DESTRO (2nd year)

Baptiste Sirjean, René Fournet

Axe CITHERE

Keywords : automatic kinetic model generator, biofuels oxidation, transition state models

General context, scientific issues :

Biofuels are a solution of choice to decrease the emission of greenhouse gas in several transport sectors, such as aviation and road freight, whose combustion engines are very difficult to replace with electric energy. However, biofuels have poor resistance to liquid phase oxidation, which deteriorates the fuel performance and safety. In this context, kinetic mechanism generators are powerful tools to understand and model the chemical mechanism behind this phenomenon [1]. These tools produce detailed models that contain thousands of species and reactions. Accurate kinetic data are essential to improve the prediction capacity and accuracy of these models.

Objectives and stakes :

The main objective of the thesis is to contribute to the development of automatic generation of kinetic model for biofuels oxidation modeling, mainly by improving the accuracy of the kinetic and thermodynamic data. Specific objectives can be listed as follow:

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

Methodology :

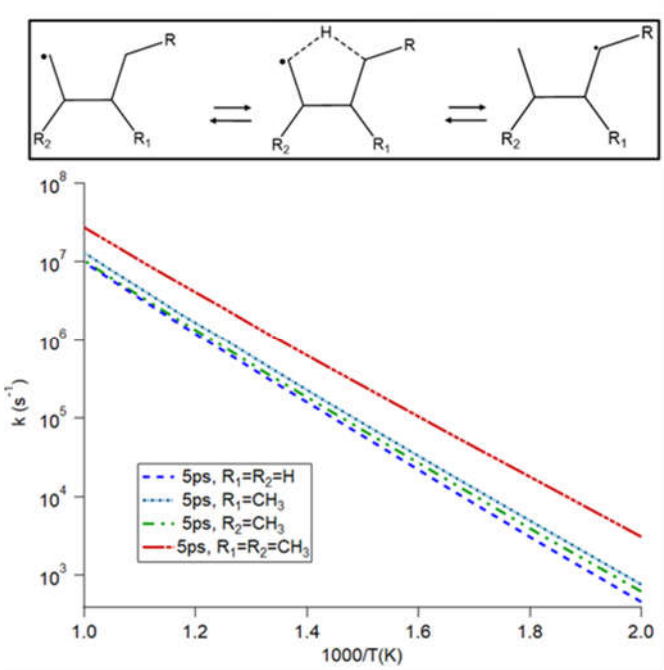
The impact of different aspects of transition state structures is investigated to create tabulated kinetic rate rules based on TS models.

- In the first stage, the degree of substitution and branching of cyclic transition state structures for intramolecular H-shift reactions were studied.

The rate rule coefficients were theoretically calculated based on the transition state theory and electronic structure calculations, adding tunneling effect and hindered rotations treatments.

- In the case of H-shift reactions with 6 and 7 membered ring TS, hundreds of cases have to be treated to englobe all the substituent combinations. Therefore, the automatization of these calculations is being developed using python code. This code starts from a non-substituted TS structure and its respective reactant and product to create all combinations and run the necessary calculations to obtain the kinetic constant for each combination of the substituted TS model.

Illustration : Impact of the R_1 and R_2 alkyl substituents on the kinetic constants of a 5-ring membered TS H-shift intramolecular isomerization



Main results

The study of TS models for intramolecular H-shift reactions showed that a rate rule based solely on the radical nature and TS cycle size is not sufficiently accurate.

Different sizes and branching levels of alkyl substituents were investigated and it was found that the influence of these aspects over the kinetic constant was minor. Therefore, a methyl substituent was suggested as a surrogate to represent alkyl group substituents. Tabulated values of kinetic constant were proposed for all combinations of substituted TS models of 1,3 and 1,4 intramolecular H-shift reactions.

For the 1,5 and 1,6 intramolecular H-shift reactions, the automated TS model calculation tool is being implemented to calculate the tabulated values for all cases.

The implementation of this tool to create TS models tabulated kinetic data for other reaction classes is envisaged as the next step.

References :

[1] M. D. Le *et al.*, *Journal of Physical Chemistry B*. **125**, 6955 –6967 (2021).

2022

Research subject : Parametric study of two-phase olive mill waste hydrothermal liquefaction

Akram DAHDOUH (2nd year)

Yann LE BRECH, Anthony DUFOUR

Axe CITHERE

Keywords : Two-phase olive mill wastes, hydrothermal liquefaction, heavy-oil, hydro-char

General context, scientific issues :

Olive oil industry generates a huge amount of wastes, either from pruning or oil extraction. The latter produces effluents with composition and properties that depend highly on the extraction methods. These generated wastes were the subject of several research papers that have proven their negative environmental impact, due to the existing phenolic compounds. Facing these environmental issues, as well as the high energy demand in the world, the Mediterranean countries must profit from the amount of wastes, with the aim to respond to their increasingly energy needs. Thus, due to the chemical composition of these effluents and their high-water content, hydrothermal process appears to be a suitable thermochemical technique for processing and recovery of this effluent to produce liquid and solid biofuels.

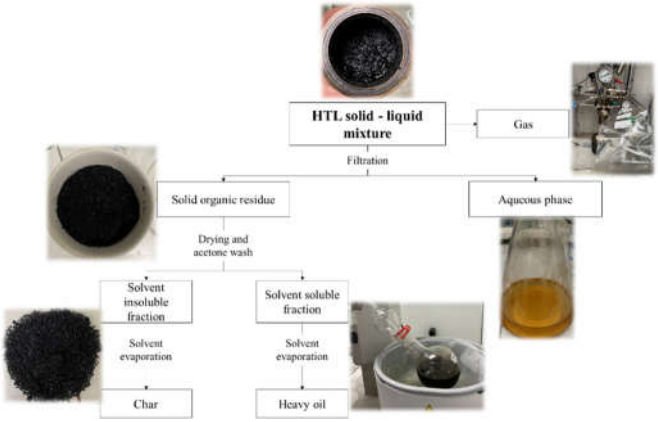
Objectives and stakes :

The aim of this study is to optimize the conversion of wet olive oil waste of Moroccan origin, mainly wastewater and pomace, by hydrothermal processes into liquid and solid fuels. This work deals, first, with the characterization of the raw materials used, then with the understanding of the effect of the operating parameters. The resulting products (hydro-chars and heavy-oils) will be characterized by different techniques and the optimum operating conditions will be identified depending on the products yields and quality.

Methodology :

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 parametric study of the process was conducted to evaluate the effect of temperature, reaction time and biomass to water ratio on the products yields and quality. The obtained products were analyzed with different techniques (Elemental analysis, Total organic carbon (TOC), Thermogravimetric analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR)).

Illustration :



Main results

The two-phase olive mill wastes hydrothermal liquefaction parametric study highlighted the impact of biomass to water ratio, reaction temperature and time on the heavy-oil and hydro-char yields and quality.

Results suggested that the optimal conditions for maximum yield and high quality for HO were different. For instance, the highest heavy-oil yield was about 37 wt.% with HHV=30.9 MJ/kg. While the highest HHV value was equal to 32 MJ/kg with yield of 34 wt.%. For process efficiency optimization, the calculated energy recovery resulted in a maximum value of 80%.

References :

[1] M. Gimenez et al., « Two phase olive mill waste valorization. Hydrochar production and phenols extraction by hydrothermal carbonization », Biomass and Bioenergy, vol. 143, p. 105875, déc. 2020, doi: 10.1016/j.biombioe.2020.105875

[2] M. Déniel, G. Haarlemmer, A. Roubaud, E. Weiss-Hortala, et J. Fages, « Optimisation of bio-oil production by hydrothermal liquefaction of agro-industrial residues: Blackcurrant pomace (Ribes nigrum L.) as an example », Biomass and Bioenergy, vol. 95, p. 273 285, déc. 2016, doi: 10.1016/j.biombioe.2016.10.012

2022

Research subject : Development of a model to simulate gaseous and particle pollutant emissions from domestic wood-burning appliances

Joseph Darido (2nd year)

Frederique Battin-Leclerc, Roda Bounaceur, Celine Le Dreff

Axe CITHERE

Keywords : Wood combustion, inset, heat transfer, modeling, soot, pollutants

General context, scientific issues :

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

Objectives and stakes :

Modify and upgrade a kinetic model (BioPOx)
Modify and upgrade the equivalent reactor network used to represent a wood burning inset in Chemkin.
Obtain numerical results for the combustion of different types of woods and study the sensitivity of some factors.
Add a chimico-physical model of soot formation.

Methodology :

The kinetic model BioPOx was optimized and validated using results from experiments done in parallel under similar conditions.
BioPOx was then coupled with an equivalent reactor network and the obtained model was validated using old studies on the oxidation and pyrolysis of individual components from the biomass.
The soot model developed by Politecnico di Milano [1] was selected and coupled to the kinetic gas phase model. Several changes were made to the obtained model to fix the reaction blocs leading to the formation of Polycyclic aromatic Hydrocarbons (PAHs). After several studies, a number of intermediate soot precursors were added to optimize this coupling, like the dibenzofuran.
After that, the ERN chain will be optimized using the results of several of the ongoing CFD studies in ANSYS Fluent [2] as shown in Illustration 2. And finally, the parameters with highest influence will be identified by a sensibility study, and several characteristics of the wood inset will be optimized, including the dimensions, the flame temperature, the wood type and moisture content.

Illustration 1 : The Equivalent reactor network (ERN)

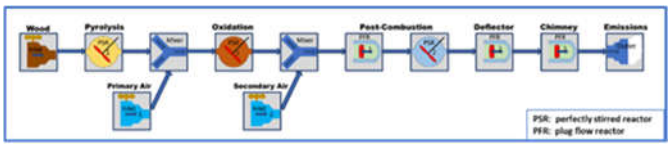
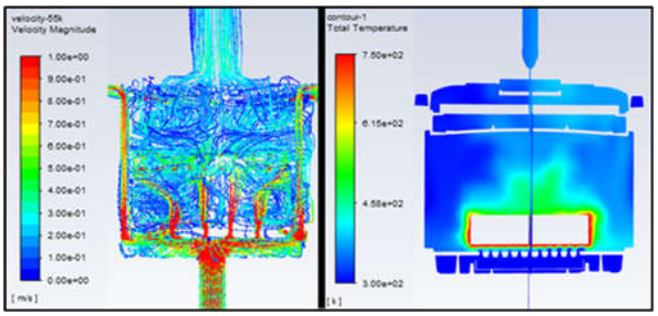


Illustration : Back view of the 3D meshed structure showing the velocities inside the inset (left). A 2D plane view of a burning log inside the wood inset colored by temperature (right). *Both calculated and colored in ANSYS Fluent*.



Main results

The used ERN, as shown in illustration 1, is divided into 6 phases: The pyrolysis phase which occurs at the surface of the log in an inset. The primary and secondary combustion phases. The deflector where the main heat exchange occurs and the chimney flue where the emission happens at its output.
The developed model simplified the heat exchanges and mass fluxes of the combustion process, and successfully reproduced the experimental trends of some measured emissions (CO, CO_2, O_2, Levoglucosan, PAH, aromatic compounds…). Studies to optimize the soot trends obtained with experimental data are ongoing, with the soot particles divided into 84 pseudo-species (BINs) of different carbon numbers and hydrogenation levels.
A detailed prediction of other expected major gaseous pollutants and soot precursors was also given by the model along with a sensitivity study showing the impact of each parameter defining the type of wood used, on the formation of these gases [3].

References :

[1] Pejpichestakul et al. Examination of a soot model in premixed laminar flames at fuel-rich conditions *https://doi.org/10.1016/j.proci.2018.06.104*
[2] ANSYS Fluent Theory Guide, ANSYS, Inc., 275 Technology Drive Canonsburg. PA 15317, November 2013

Published work

[3] Darido, J., Dhahak A. et al., Emissions from a domestic wood heating appliance: Experimental measurements and numerical study using an equivalent reactor network (ERN) approach coupled with a detailed chemical mechanism. *Energy Fuels* **2021**, *35*, 18680– 18698, *https://doi.org/10.1021/acs.energyfuels.1c01927*

2022

Research subject : Combustion performances of biofuels resulting of Enzymatic Hydrolysis Lignin

Nicolas Delort (2nd Year)

Frédérique Battin-Leclerc, Olivier Herbinet, Roda Bounaceur

Axe CITHERE

Keywords : combustion, biofuel, lignin, flame, detailed kinetic model

General context, scientific issues :

In a context of global warming and exhaustion of fossil sources of energy, the role of science and engineering is to study and develop new technologies to contribute to the energy transition in order to reach carbon neutrality. Transport is one of the bigger emitters of greenhouse gas: 25% in 2019; 29% of final energy is consumed in this field [1]

Objectives and stakes :

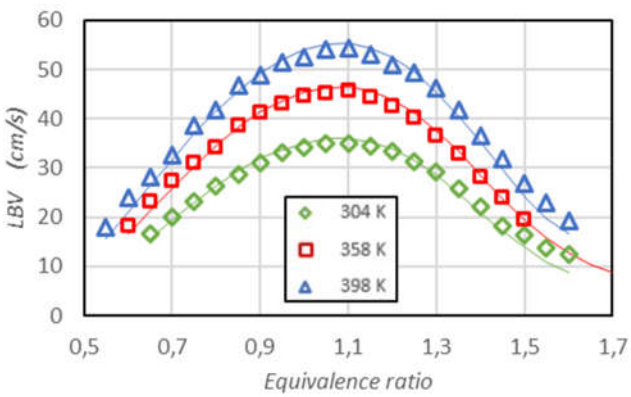
The European project EHLCATHOL [2] aims to develop a new kind of 2G biofuel synthesized from EHL, a waste of 2G bio-ethanol refineries. It gathers Universities (AALTO, LIKAT, EPFL, NTNU, TU/E, LRGP-CNRS) and an industrial partner (Vertoro). Our team in Nancy is in charge of the combustion study with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

Methodology :

The methodology is to separately work on the biofuel compounds, arenes and oxygenated aromatics, the combustion properties of the biofuel are then interpolated.
The tasks on which I am involved are the measurement of Laminar Burning Velocities (LBV), the development of a detailed kinetic model (DKM), the prediction of ignition properties (CN/RON) and Lower Heating Values.

- LBV are measured 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 is one of the last developed apparatus, its main advantage is the direct way to obtain the LBV value.
- The DKM allows to model the combustion on Chemkin Pro. The basis of this DKM is a merge of Curran [4] and Yuan [5] model to allow a good precision and a good numerical convergence. Blocks for other aromatics will be then added. This developed DKM is validated with experimental literature data and the ones established by our team (species profiles in JSR and LBV).
- RON and CN are non-linear properties, rarely studied for our compounds of interest. A bibliographical work was performed to evaluate the predictive methods.

Illustration : Experimental and modeling results of LBV of toluene
symbols are experiments and lines are simulation



Main results

LBV measurements are performed with toluene, 3 xylene isomers, styrene, 2 trimethylbenzene isomers, anisole and acetone. Results are in accordance with literature data; some experiments were also achieved in new conditions that extend the available database.

The DKM for toluene, base of the aromatic mechanism, has been built. The numerical results on toluene kinetics are in good agreement with our team's experimental data and literature one. Even for aromatics LBV, numerical convergence is excellent despite the size of the mechanism

References :

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

[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] U. Burke, J. Beeckmann, W.A. Kopp, Y. Uygun, H. Olivier, K. Leonhard, H. Pitsch, K.A. Heufer, A comprehensive experimental and kinetic modeling study of butanone, Combustion and Flame. 168 (2016) 296–309. https://doi.org/10.1016/j.combustflame.2016.03.001.

[5] W. Yuan, Y. Li, P. Dagaut, J. Yang, F. Qi, Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation, Combustion and Flame. 162 (2015) 3–21. https://doi.org/10.1016/j.combustflame.2014.07.009.

2022

Research subject : Hydrogen Production from Biomass and Waste Gasification: Modeling, Techno-Economic & Environmental Assessment of Innovative Solutions

Rémi DEMOL (Postdoc)

Guillain MAUVIEL, Yann ROGAUME

Axe CITHERE | LERMAB

Keywords : gasification ; biomass ; waste ; techno-economic assessment ; process simulation ; environmental assessment ; reactor model

General context, scientific issues :

To mitigate climate change, a fast development of renewable energies is required. In France, wood is the first renewable energy used mainly for local heat production [1]. It is also technically feasible to produce electricity from wood gasification i.e., the partial oxidation of the feedstock into a synthetic gas. This syngas is mainly made of H_2, CO, CO_2, CH_4 and hydrocarbons. However, a lot of undesired species, such as tars, are also created requiring subsequent cleaning steps and penalizing the economic viability of the process [3]. Renewable hydrogen is produced during the process and can be separated and valorized. Biomass and waste gasification is identified by the French environmental agency (ADEME) as a potential major supplier of renewable gas for the next decades [2].

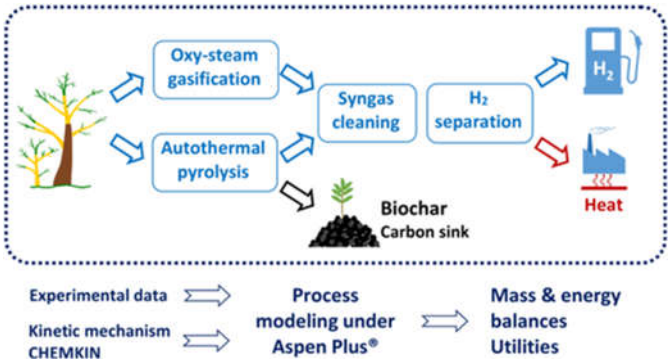
Objectives and stakes :

This project models and compares different processes designed to produce hydrogen, heat and biochar on an economic and life cycle basis.

Methodology :

To get detailed data to build the techno-economic assessment, process simulation software are powerful tools. Several unit operations along a process are combined [4,5], particularly with the downstream gas cleaning process [3]. These simulations provide heat and mass balance required for the estimation of CAPEX and OPEX and also for the life cycle assessment (LCA). This project focus on a small unit of 20 megawatts of biomass input. This scale seems more appropriate for the smaller area of supply required and for social acceptability purpose (LHV basis). This project tends to maximize the efficiency by upgrading multiple products: heat, hydrogen and biochar, to overcome the small size of the unit. A life cycle assessment is done to evaluate the global impact of the different options investigated. Under few assumptions, pyrogasification could be carbon neutral or even carbon negative, when biochar is produced [6].

Illustration :



Main results

Along this project the main findings are

- The development of a **partial oxidation unit model** with a radical kinetic mechanism on Chemkin validated on experiments and coupled with Aspen Plus.
- The development of a **hybrid process to separate hydrogen** from a wood gasification syngas.
- The **detailed modeling of three processes** of hydrogen, heat and biochar production from wood. Estimation of mass and heat balances for a 20 MW-scale unit and its utilities and consumable consumption [7].
- The **comparison of these processes on economic and environmental basis**. The production of hydrogen from wood is ten times less emissive of warehouse gases than steam methane reforming. Subsidies are required to reach profitability in the market past conditions (120-210 €/t CO_2 avoided), unless the natural gas price remains permanently high. A potential carbon sequestration is able with the pyrolysis process.

References :

[1] ADEME. Les énergies renouvelables en France (2016)
[2] ADEME. A 100% renewable gas mix in 2050? (2018).
[3] Woolcock et al. *Biomass and Bioenergy* **52**, 54-84 (2013).
[4] Francois *et al. Biomass and Bioenergy* **51**, 68–82 (2013).
[5] Pauls et al. *Biomass and Bioenergy* **95**, 157–166 (2016).
[6] Dufour. *Environmental Science & Technology* (2013).
[7] Demol et al. *Energy & Fuels* **36**, 488-501 (2022).

2022

Research subject : Multi-scale approach for working fluids modelling in waste heat revalorisation processes

Thomas DI PIETRO (3rd year)

Fabrice Mutelet, Laëtitia Cesari

Axe CITHERE

Keywords : Thermodynamics, energy, heat pump, modelling, deep eutectic solvents

General context, scientific issues :

Industries produce a significant amount of waste heat, usually rejected in the atmosphere but potentially exploitable in the context of the increase in energy demand. Among existing technologies, absorption heat pumps can be used for heating as well as for cooling (air conditioning or refrigeration). Unfortunately, traditional working fluids (Water/Lithium Bromide or Ammonia /Water) display numerous drawbacks (corrosion, toxicity, risk of crystallization) which hinder the development of these technologies

Objectives and stakes :

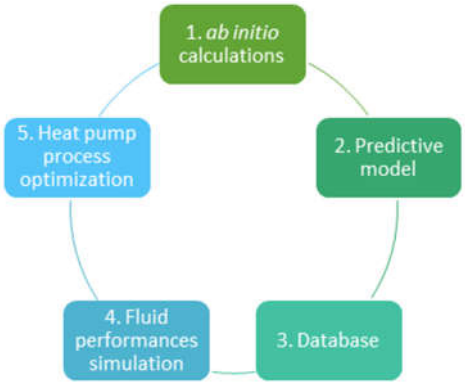
As an alternative to classical working fluids, new solvents ought to be less toxic and at least as effective. Among those investigated, Ionic Liquids (ILs) and Deep Eutectic Solvents (DESs) are of interest. Indeed, they display tunable physical and chemical properties which can be easily altered by changing the components of the DES or the structure of the cation or anion of the IL. However, the behavior of these solvents with other fluids is still little known. Thus, in this study the investigation of {IL/DES-water} mixtures as a part of a heating process using heat transformers is considered. The aim of this work is the evaluation of the performances of the fluids in absorption heat transformers and the optimization of the process

Methodology :

The infinite number of ILs and DESs makes quite inconceivable the measurements of the properties of all pure ILs/DESs and of their mixtures with other fluids. Accordingly, the development of predictive models requiring no experimental data is essential. To do so, an innovative method based on a multi-scale approach is investigated.

A microscopic study by means of ab initio calculations allows to gain insight on the influence of the structure of various components on the different interactions involved in the working materials. This way, stable molecular arrangements are determined and then fed to a predictive and robust thermodynamic model. This model can finally be integrated into a simulation software to design and optimize processes

Illustration : Methodology for the choice of working fluids in absorption heat pump processes



Main results

Ab initio calculations were performed with Gaussian 09 to provide descriptors of a reference state for molecules in a virtual conductor.

Based on the Conductor-like Screening Model (COSMO), COSMO-RS[1] and COSMO-SAC[2] methods make use of these descriptors to predict the activity coefficients γ_i of molecules of interest in a mixture. They combine statistical thermodynamics and quantum chemical calculations and take into account different energies of interactions (such as hydrogen bonds) related to the molecules being back in a real conductor.

Parameters were optimized for a better representation of the hydrogen bonds in mixtures involving halogens. Activity coefficients of various systems were computed for given temperatures and compositions. This enables to predict vapour-liquid, liquid-liquid and solid-liquid equilibria of {water + IL/DES} mixtures. When compared to vapor-liquid experimental data, the accuracy of the predictions are improved by around 10%.

References :

[1] Klamt, A. Jonas, V., Bürger, T., Lohrenz, J. C. W., 1998. Refinement and Parametrization of COSMO-RS, J. Phys. Chem., 102, 5074-5085

[2] Bell, I. H., Mickoleit, E. Hsieh, C.-M., Lin, S.-T., Vrabec, J., Breitkopf, C., & Jäger, A., 2020. A Benchmark

2022

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

Timothée FAGES (1st year)

Pierre-alexandre Glaude, René Fournet

Axe BIOPROMO

Keywords : Gasoline, alcohol, soot, biofuels Gasoline, alcohol, soot, biofuels

General context, scientific issues :

Despite the growth of the electric vehicle fleet, spark-ignited (SI) petrol engines will still account for at least 50% of light vehicles over the next decade. Direct injection (DI) SI engines provide substantial fuel economy. Yet, they also emit a significant amount of soot caused by the combustion of the fuel film that settles on its walls.
The European Union (EU) favors the use of oxygenated biofuels in vehicles, which tend to reduce soot emissions. However, they can increase the emission of other particles such as aldehyde and NOx.

This study aims at predicting the various types of particles emitted.

Objectives and stakes :

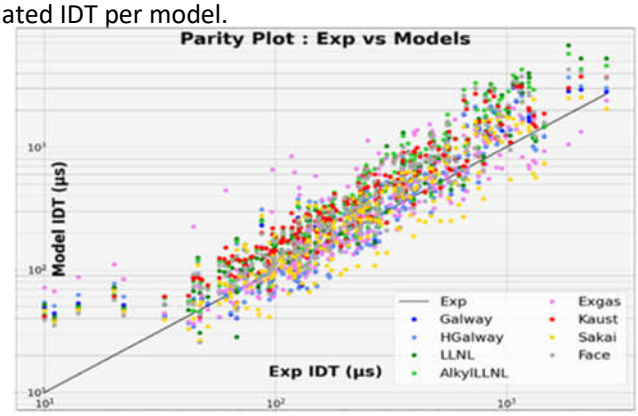
The purpose of this project is to model and simulate soot and pollutants formation from biofuels when used in DI-SI engines to inform the development of a low emission motor. The detailed kinetic model of the oxygenated gasoline combustion should be able to predict the main combustion parameters and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

Methodology :

The oxygenated gasoline will be modeled with isooctane, n-heptane, toluene and either ethanol or isobutanol to make it computationally usable.
Different kinetic models from the literature will be tested, modified, and reduced through the utilization of the Ansys Chemkin-Pro software or the Cantera Python module. This will comprise
* The comparison between experimental and simulated ignition delay times (IDT) in a shock tube.
* The comparison between experimental and simulated species profiles and 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

Illustration : : Parity plot between experimental IDT and simulated IDT per model.



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 AlkylLLNL

Table 1 : Mean absolute relative errors of simulated IDT and BV compared to experimental values

	Galway	HGalway	LLNL	AlkylLLNL	Exgas	Kaust	Sakai	Face
Average IDT	39%	81%	56%	63%	200%	74%	56%	55%
Average BV	/	8,7%	9,1%	8,5%	/	6,7%	/	/

Over the range of IDT (821 experimental points) and the BV studied (table 1), the best mechanism so far seems to be the Galway mechanism. 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 AlkylLLNL (6500/1500) have relatively close results and have not yet been reduced. Therefore, by improving those small models, we may achieve a model that is more computationally usable than Galway

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

2022

Research subject : Study of the pyrolysis of plastic waste: experimentation and modeling

Nabil Hassibi (2nd year)

Valérie VITZTHUM, Guillain MAUVIEL

Axe *CITHERE*

Keywords : Pyrolysis, plastic waste, reflux, modeling

General context, scientific issues :

The amount of plastic consumption is increasing every year worldwide. The waste generated by their production, transportation and disposal creates various environmental problems. Within the different ways of using plastic waste, pyrolysis seems to be an attractive and environmentally friendly possibility for a sustainable use of waste in the long term [1], [2].

The products obtained by the pyrolysis of plastics depend generally on the evolution of the temperature of the plastic, the use of reflux, the type of reactor, the pressure, the residence time of the solid and the gas, the catalysts, the type and the ratio of carrier gas flow to the plastic flow [3]

Objectives and stakes :

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

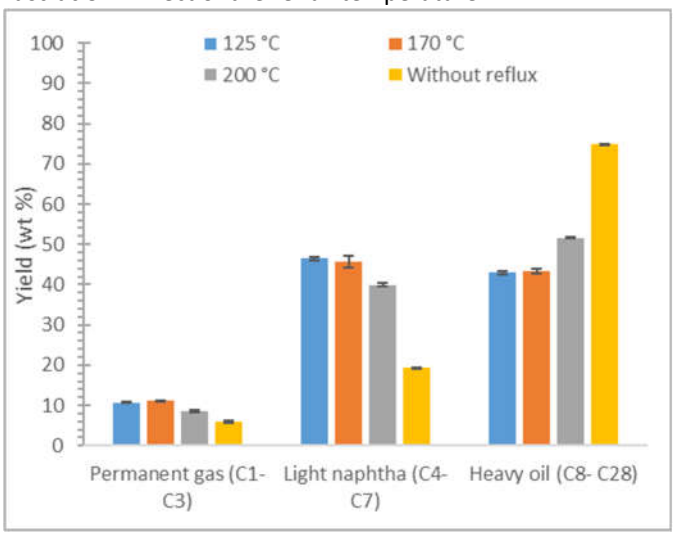
Methodology :

The experimental work related to this thesis started on a small, well-controlled reflux semi-batch reactor with a polyolefin (polypropylene), before working on a semi-industrial pilot. These tests are explored at various conditions (pure or mixed polymer, heating power, inert gas flow). The various products are characterized (gas by online micro-GC, oils by GC-FID-MS).

Main Objective :

One of the main objectives of this PhD thesis is to study the influence of a reflux in order to obtain and maximize the production of hydrocarbons with a narrow distribution of light molecular weight (MW) compounds which are more highly valuable, especially those corresponding to the naphtha cuts (light naphtha with 4–7 carbon atoms and heavy naphtha with 8–12 carbon atoms).

Illustration : Effect of the reflux temperature



Three temperatures of reflux have been tested: 125°C, 170°C and 200°C. The effect of reflux temperatures on the yield of liquid product and gaseous product were studied and compared with pyrolysis experiments without reflux. The products were qualitatively and quantitatively analyzed by different techniques.

Main results

The importance of the use of a reflux to control products composition and to narrow the molecular weight distribution of the valuable compounds (naphtha cuts) were successfully demonstrated in this study even if the temperature range used did not have that much influence on the distribution of the products

References :

[1] N. Kiran, E. Ekinci, et C. E. Snape, « Recyling of plastic wastes via pyrolysis », *Resources, Conservation and Recycling*, vol. 29, n° 4, p. 273-283, 2000.

[2] O. Dogu *et al.*, « The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions », *Progress in Energy and Combustion Science*, vol. 84, p. 100901, 2021.

[3] W. Kaminsky, « Possibilities and limits of pyrolysis », *Makromolekulare Chemie. Macromolecular Symposia*, vol. 57, n° 1, p. 145-160, 1992

2022

Research subject : Application of High Precision Absorption Spectroscopy Techniques for the Quantification of Intermediates and Radicals in Biofuel Combustion Chemistry

Caroline Smith Lewin (1st year)

Frédérique Battin-Leclerc, Jérémy Bourgalais

Axe CITHERE

Keywords : low-temperature combustion, ozone-assisted oxidation, jet-stirred reactor, chemical kinetics, gas chromatography, mass spectrometry

General context, scientific issues :

Technological innovations for more economical and ecological internal combustion engines require a knowledge of the elementary reactions governing the auto-ignition and oxidation of hydrocarbons and biofuels, especially at low temperatures (< 1000 K).

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

Objectives and stakes :

- Investigation of the O_3-assisted oxidation of alkenes by gas chromatography (GC) and mass spectrometry (MS) in a jet-stirred reactor (JSR).

- Coupling of the JSR with cavity ring down spectroscopy (CRDS) and cavity enhanced optical frequency comb spectroscopy to measure intermediates and radicals of the low temperature combustion chemistry.

Methodology :

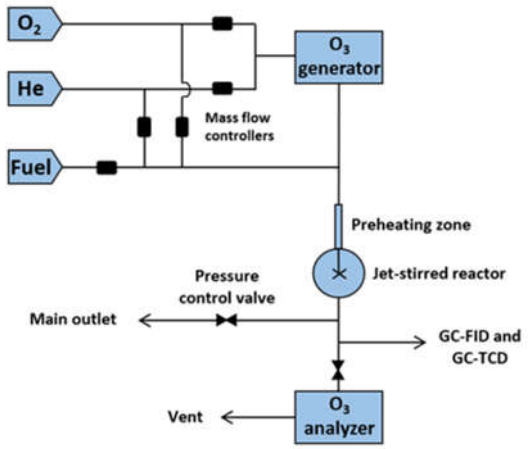
An illustration of the experimental setup used for GC measurements is provided.

Constant pressure, residence time, and equivalence ratio of 800 Torr, 2.5 s, and 0.5, respectively, were maintained for all the experiments. Preheating upstream of the JSR was performed, but up to 393 K to prevent the thermal decomposition of O_3 before entering the reactor.

The oxidation of ethylene (C_2H_4) and 1-hexene (C_6H_{12}) was investigated under dilute conditions, with and without O_3 (up to 2000 ppm).

When available, chemical kinetic models[1,2] were used for simulations in CHEMKINPro, and their results were compared with the experimental ones obtained in this study.

Illustration : Scheme of the experimental setup



Main results

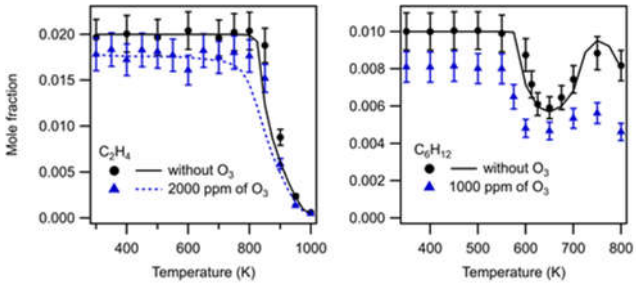
The thermal decomposition of O_3 starts ~450 K and ~90% of O_3 is consumed by 550 K.

O_3 addition enables a fuel conversion of ~10% and ~20% for C_2H_4 and C_6H_{12}, respectively, in the low temperature regime (from ~350 K).

O_3 enhances as well the production of formaldehyde (CH_2O), methanol (CH_3OH), acetaldehyde (CH_3CHO), oxirane (C_2H_4O), carbon monoxide (CO), and carbon dioxide (CO_2).

The initial ozonolysis reaction, therefore, shifts the temperature window of the conversion of the fuel and product formation to a lower temperature regime, in which the traditional oxidation cannot be initiated

Fuel consumption as a function of temperature



References :

[1] Shen, X., Yang, X., Santner, J., Sun, J., & Ju, Y. (2015). Experimental and kinetic studies of acetylene flames at elevated pressures. *Proceedings of the Combustion Institute*, 35(1), 721-728

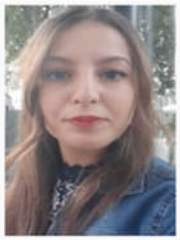
2022

Research subject : Experimental study of the low-temperature oxidation of the three isomers of xylene in a jet-stirred reactor

Ismahane MEZIANE (2nd year)

Olivier Herbinet, Frédérique Battin-Leclerc

Axe CITHERE



Keywords : Combustion, Low- temperature oxidation, Enzymatic hydrolysis lignin, Bio-oils, Jet-stirred reactor, Chemical kinetics

General context, scientific issues :

LRGP-CNRS is involved in the EHLCATHOL[1] project since November 2020. EHLCATHOL is a European project that aims to develop a new kind of second-generation (2G) biofuel synthesized from Enzymatic Hydrolysis Lignin (EHL), a by-product of 2G bio-ethanol refinery. These liquid fuels are intended to be used as alternative fuels, as they are generated from renewable and sustainable sources with a low CO_2-emission. To achieve the objectives of this project, I perform laboratory experiments and develop detailed kinetic models.

Objectives and stakes :

- Characterize the intrinsic reactivity of these fuels
- Set up one- and two- dimensional gas chromatography (GC) methods to identify and quantify the reaction products.
- Establish a comprehensive experimental database of the combustion products for this class of fuels.

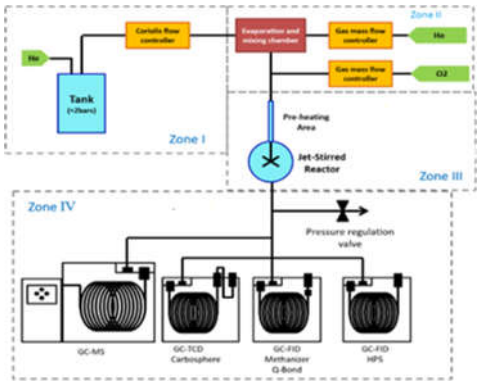
Methodology :

Bio-oils can be made from biomass, especially lignocellulosic biomass. Biomass is mainly composed of three polymers: cellulose, hemicellulose, and lignin. In addition, EHL is a by-product of the bioethanol production process[2].

The oxidation experiments were carried out in a jet-stirred reactor operating under dilute conditions. The identification and quantification of the products were achieved using mono-dimensional GC with a mass spectrometry (MS) and a flame ionization detector (FID).

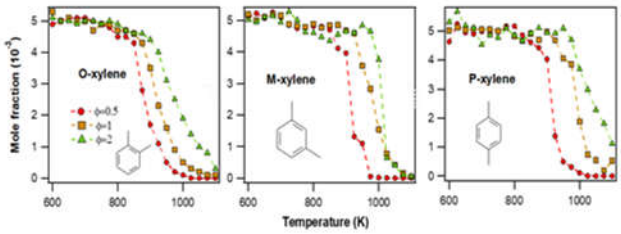
Experiments have already been performed on guaiacol, toluene, the three isomers of xylene and acetone which is one of the solvents used in the manufacturing process. In addition, it is planned to study the oxidation of phenol, o-, m-, p-cresols, and other complex samples provided by the members of the EHLCATHOL consortium.

Illustration : Schematic of the experimental set-up



Main results

The experimental results obtained in this study showed a start of the reactivity at 700, 750 and 825 K for ortho, meta -, and para-xylenes, respectively. Main products of the three isomers are CO, CO_2, benzene, toluene, benzaldehyde, methyl-benzaldehyde and benzofuran. Methyl-benzaldehyde is the major product below 800 K and the formation of phtalan (o-xylene oxide), a cyclic ether linking the two alkyl branches observed in the case of o-xylene, as proposed by Roubaud et al[3]. during their work in a rapid compression machine, was also identified in the present work.



Conversion of ortho-, meta-, and para-xylene during their oxidation in a JSR (work in progress).

References :

[1] http://ehlcathol.eu/

[2] Jin, Y., Ruan, X., Cheng, X., & Lü, Q. (2011). Liquefaction of lignin by polyethyleneglycol and glycerol. *Bioresource Technology*, *102*(3), 3581-3583.

[3] Roubaud., O Lemaire., R Minetti., L.R Sochet (2000). High pressure auto-ignition and oxidation mechanisms of o-xylene, o-ethyltoluene, and n-butylbenzene between 600 and 900 K, 123(4), 561–571.

2022

Research subject : Design of power cycles for sustainable electricity generation

Michel Molière (2nd year)

Romain Privat, Jean-Noël Jaubert

Axe CITHERE

Keywords : Power generation, supercritical fluid, CO2, Rankine cycle, Brayton cycle

General context, scientific issues :

The way towards sustainable power generation requires the exploration of novel cycles that might enable a strong increase in efficiency and decrease of fossil fuel consumptions as well as CO_2 emissions

Objectives and stakes :

Explore novel supercritical CO_2 based power cycles.

The stake is the identification of high efficiency cycles to be potentially applicable to convert high-temperature or residual heat fluxes into electricity .

Methodology :

The adopted methodology consists in the following steps:

1- Acquiring the basic knowledge of the specifics of the thermodynamics of supercritical CO_2 cycles (sCO_2) along with the use of the dedicated simulation software items (i.e.: Simulis Thermodynamics & PROSIM Plus Energy).

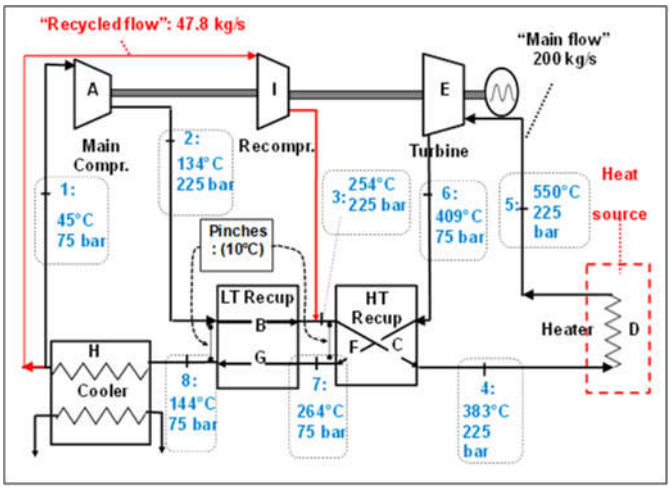
2- Exploring the capabilities and limits of Rankine sCO_2 cycles

3- Focusing on the capabilities of Brayton sCO_2 cycles

4- Making comparisons between the energy performances of the best sCO2 Brayton cycles with those of conventional steam Rankine ones.

Since an experimental approach of this topic cannot be envisaged, due to the far-reaching equipment items that would be required and the multiplicity of the possible cycle configurations, the studies of the sCO_2 Brayton cycles is being performed based on purely numerical simulations.

Illustration : sCO2 Brayton cycle with Recompression



Main results

A thorough analysis of the performances of selected configurations of sCO_2 Brayton power cycles highlights remarkable intrinsic efficiencies, up to 48%, in applications where the heat sources are substantially isothermal, i.e. the temperatures of which are constant within some 100-150 °C. This quality makes them potential technologies of choice for solar or future nuclear power units.

However, in waste heat recovery applications, two-pressure steam cycles outperform sCO_2 ones, even those equipped with a double heat recovery and this is namely due to a better ability of liquid water to transfer thermal energy from the topping cycle to the bottoming one. However, the comparison is not entirely consistent as the steam cycle involves more heat recovery exchangers.

Finally, semi-closed, oxygen fired sCO_2 cycles with inherent CO_2 capture represent a technology breakthrough

References :

1] M. Molière, R. Privat, J.N. Jaubert at al., congrès SFT 2022, Production thermique d'électricité et cycles thermodynamiques alternatifs, Valenciennes, 30 Mai/3 Juin 2022

2] Ibidem, Emerging Thermodynamic Cycles and Thermal Power Generation, ECOS 2022 Congress, Copenhagen, 3-7 July 2022

2022

Research subject : High pressure and temperature hydrothermal conversion of lignocellulosic biomass

Saad NADER (Post-doc)

Anthony DUFOUR, Yann LE BRECH

Axe CITHERE

Keywords : Biomass, hydrothermal treatment, Thermodynamic, Phenolic compounds, carbohydrates

General context, scientific issues :

With the growth of environmental concerns, researchers are focusing on the replacement of oil-based products by bio-based ones to reduce the climate change impacts. Lignocellulosic biomass is the most abundant source of renewable polymers on earth. Lignocellulosic biomass (wood, bark, straw, etc.) is composed mainly of cellulose (40-60 wt %), hemicelluloses (20-40 wt %), and lignin (15-25 wt %). Valorization of these three compounds presents an environmentally friendly promising source of renewable carbon.

Objectives and stakes :

The aim of this project is to study:

- Physico-chemical hydrothermal conversion mechanisms with original solid and liquid analysis methods.

- Biomass conversion processes at different scales

Methodology :

Hydrothermal treatment at high pressure and temperature is applied on different biomasses.

The follow-up of the conversion reactions of the different species is studied using different analytical methods (HPLC, ionic chromatography, etc.)

Main results

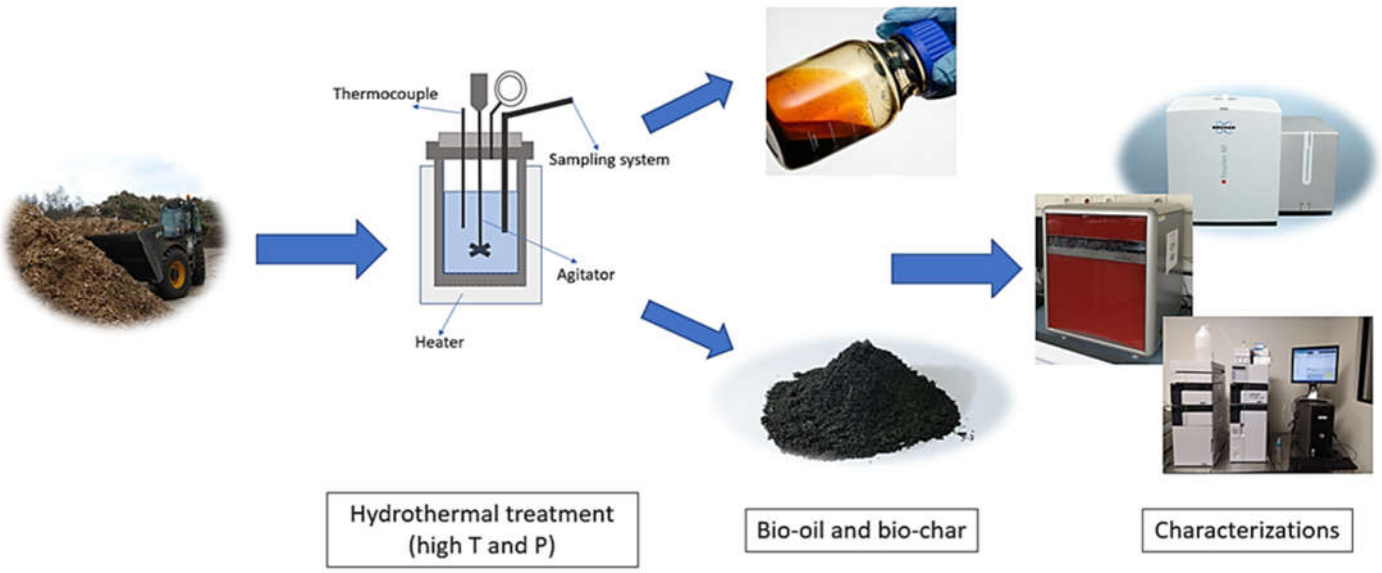
Due to some technical problems, results are still under processing

References :

[1] E. Bartolomei, Y. Le Brech, A. Dufour, V. Carré, F. Aubriet, et al.. Lignin Depolymerization: A Comparison of Methods to Analyze Monomers and Oligomers. ChemSusChem, ChemPubSoc Europe/Wiley, 2020, 13 (17), pp.4633-4648. ff10.1002/cssc.202001126ff. ffhal-02900733f

[2] F. Buendia-Kandia, G. Mauviel, E. Guedon, E. Rondags, D. Petitjean, et al.. Decomposition of cellulose in hot-compressed water: detailed analysis of the products and effect of operating conditions. *Energy and Fuels*, American Chemical Society, 2017, 10.1021/acs.energyfuels.7b02994. hal-01651273

Illustration :



2022

Research subject : Study of new working mixtures containing deep eutectic solvents for absorption heat transformers

Fatima Zohra NESSAKH (4th year)

Fabrice MUTELET, Amina NEGADI

Axe CITHERE

Keywords : Energy, thermodynamic properties, absorption heat transformer, deep eutectic solvents, efficiency evaluation, simulation.

General context, scientific issues :

In recent years, industrial and domestic activities increased oil and fossil fuel demand while fossil fuel supplies of the world are limited and the fuel reserves are getting depleted. Moreover, environmental problems represented by the greenhouse effect and increasing CO_2 emissions have been rapidly thrust upon us. Therefore, we observed a growing interest in energy efficiency, increasing general interest in energy conservation and development of alternative energy sources such as solar energy. Researchers are interested in developing equipment that facilitate the recovery and efficient use of energy. It was found that absorption heat pumps are considered as a suitable solution for a rational use of waste heat, in more specific details, the Absorption Heat Transformer AHT.

Recently deep eutectic solvents (DESs) have been presented with an important interest as the ionic liquids. Moreover, DESs possess attractive physicochemical properties such as a wide range of liquids, inflammability and negligible vapor pressure (nonvolatile), high ionic conductivity, high solubility, biodegradability, chemical and thermal stability, making them highly acceptable as solvents, catalysts and absorbers for various applications [1], [2]

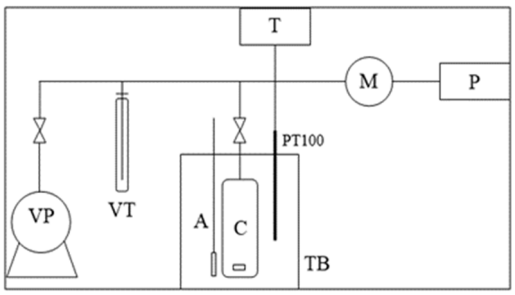
Objectives and stakes :

In this work, the thermodynamic properties of the pure DESs and its mixture with water and ethanol will be measured. Among others, vapor-liquid equilibria, excess molar volume, excess molar enthalpy and heat capacity we will determine in a large range of temperature and pressure. Then, Experimental data will be used to evaluate the performance of such fluids in AHT

Methodology :

In this work, the density of (Glyceline + water) and (Glyceline + ethanol) were measured over the full range of composition in a large range of temperature using the ANTON Paar density meter DMA™ 4500 M. The VLE measurements of binary systems have been performed in the temperature range from 298.15 K to 333.15K using a static method. The apparatus used is presented in the illustration. Excess enthalpy of the binary mixture for both binary systems were measured at 298 K using a SETARAM C80 calorimeter.

Illustration : Schema of the VLE apparatus: VP: Vacuum Pump; VT: Vacuum Trap; A: Magnetic stirrer; C: Equilibrium Cell; PT-100: Platinum resistance Thermometer; T: Temperature Indicator, M: Calibrated Pressure Sensor, P: Digital Pressure Indicator and TB: Thermostatic Bath



Main results

A bibliographic study had the main objective to collect the thermodynamic data of various DES and their mixture in order to define the most efficient systems for the heat pumps. It was found that DES composed of choline has interesting thermodynamic properties.
Excess properties (V^E and H^E and Cp^E) were determined for working fluids containing {DES + water}. The studied fluids showed a negative deviation from Raoult's low which confirm existence of the unlike interactions between the absorbent and the refrigerant. All these thermodynamic properties were used to evaluate the efficiency of these working fluids in absorption heat transformers. As we noticed from the experimental data, the new fluid (H_2O/DES) showed similar performance to ionic liquids [3] but they have a COP slightly lower than conventional working fluid (H_2O/LiBr).

References :

[1] T. El Achkar, H. Greige-Gerges, et S. Fourmentin, « Basics and properties of deep eutectic solvents: a review », *Environ. Chem. Lett.*, vol. 19, n° 4, p. 3397-3408.

[2] I. Wazeer, M. Hayyan, et M. K. Hadj-Kali, « Deep eutectic solvents: designer fluids for chemical processes », *J. Chem. Technol. Biotechnol.*, vol. 93, n° 4, Art. n° 4, avr. 2018.

[3] E.-S. Abumandour, F. Mutelet, et D. Alonso, « Performance of an absorption heat transformer using new working binary systems composed of {ionic liquid and water} », *Appl. Therm. Eng.*, vol. 94, p. 579-589, févr. 2016.

2022

Research subject : high-throughput thermodynamic methods combined with oxidation stability models of sustainable biofuels.

Francisco Carlos Paes (1st year)

Romain Privat, Baptiste Sirjean

Axe CITHERE

Keywords : : thermodynamics, kinetics, modeling, equation-of-state, quantum chemistry method (COSMO)

General context, scientific issues :

Aging of biofuels relies on a complex free-radical oxidation mechanism involving thousands of reactions and chemical species. The detailed oxidation kinetic models are based on gas phase mechanisms that are adapted to the liquid phase through a correction that depends on the solvation Gibbs energy $(\Delta_{solv}\bar{g}_i)$ of each specie involved. However, there is a lack of reliable and high-throughput solvation models that can handle radical species.

Objectives and stakes :

In this framework, the objective of this study is to devise a method for calculating the solvation quantities of radicals.

Methodology :

$$\overbrace{XH}^{\text{Parent Molecule}} \longrightarrow \overbrace{X\square}^{\text{Radical}} + \overbrace{\square H}^{\text{Hydrogen}}$$

For a given parent molecule XH, $\Delta_{solv}\bar{g}_{XH}$, can be predicted by cubic Equation-of-State, (cEoS). Our group has implemented the UMRPRU cEoS.

$$\Delta_{solv}\bar{g}_i^{XH,\infty}(T,P) = RT\ln\frac{P\,\overbrace{\varphi^{\infty}_{XH,liq}(T,P)}^{\text{solute fugacity}}}{RT\,\underbrace{\rho^{sat}_{liq}(T,P)}_{\text{liquid density}}} \quad (1)$$

For its radical X•, a correction term is added, as shown in Equation 2. The σ-moment approach was used for this purpose. This method stands for an empirical extension of the COSMO-RS solvation model

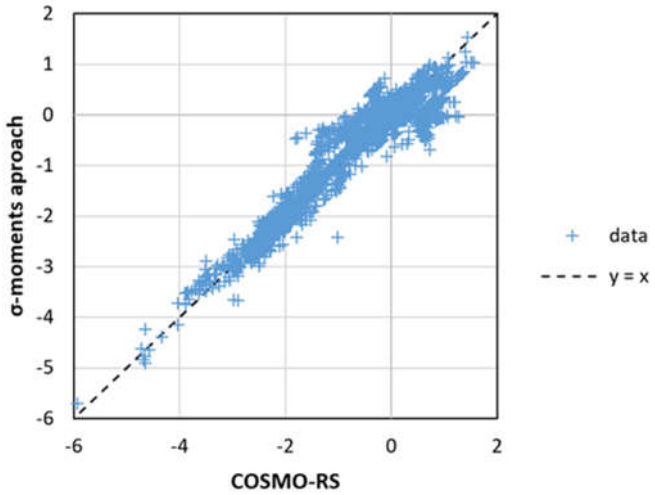
$$\underbrace{\Delta_{solv}\bar{g}_S^{X\square,\infty}}_{\text{Radical}} = \underbrace{\Delta_{solv}\bar{g}_S^{XH,\infty}}_{\substack{\text{Parent molecule}\\ \text{(UMRPRU EOS)}}} + \underbrace{\Delta\Delta_{solv}\bar{g}_S^{XH,X\square,\infty}}_{\substack{\text{correction term}\\ \text{(COSMO-based simplification)}}}$$

(2)

COSMO-RS uses as input the density charge distribution obtained from time-consuming quantum chemistry methods that are performed for each molecule.

The σ-moment approach only considers the moments of these highly localized charge distributions.

Parity plot: $\Delta\Delta_{solv}\bar{g}_{XH,X\cdot}$ [kcal/mol] at 298K



Main results

At first, a benchmarking involving the different approaches dicussed fo far (EoS and COSMO) was done over a dataset of more than 60,000 experimental points of binary mixtures at infinite dilution (only parent molecules). We obtained the following deviation results for $\Delta_{solv}\bar{g}_{XH}$:

Model	Average absolute deviation [kcal/mol]
COSMO-RS	0.31
COSMO-SAC	0.38
PSRK cEoS	0.31
UMRPRU cEoS	0.35

This indicates that the first term of Equation 2 can be well-predicted using either of the methods above.

Afterwards, a database for the correction term was generated using COSMO-RS. This database involves all the combinations between 60 radicals and 80 solvents.

The pseudo-experimental points from this database were than calculated using the method of moments, and the results are shown in the parity plot above.

A good correlation was obtained between calculated and pseudo-experimental data, since the average absolute deviation was around 0.2 kcal/mol

The moments were obtained directly from the charge density distributions. The next step is to develop a GCM to predict their value.

References :

[1] A. Jalan, R.H. West, W.H. Green, J. Phys. Chem. B.

2022

Research subject : : Pyrolysis and oxidation of a scramjet fuel

Boris Roux (1st year)

René Fournet, Y. Simon

Axe CITHERE

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

General context, scientific issues :

As expressed in its scientific security plan [1], ONERA (Office national d'étude et de recherche dans l'aérospatial) has decided to make research on hypervelocity propulsion a priority. To achieve its objectives, ONERA is working with MBDA on propulsion, aerodynamics and materials aspects, for high-speed vehicles powered by supersonic combustion ramjet (scramjet). This thesis is a part of all the research made about the combustion of a scramjet fuel.

Objectives and stakes :

In this thesis, the main goal is to develop a combustion mechanism for both pyrolysis and oxidation of a scramjet fuel. This mechanism will be validated against experimental results obtained during the PhD or a literature review.

Methodology :

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

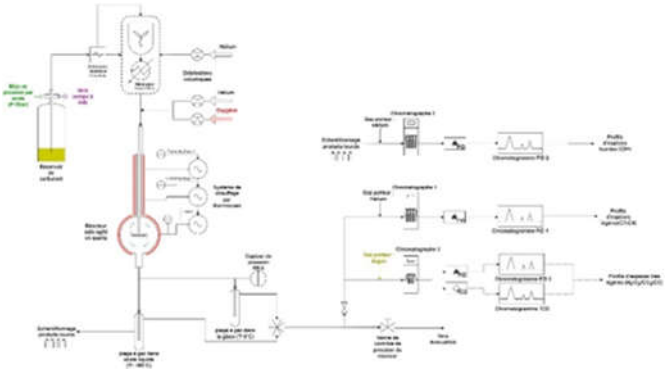
1.Determination of the fuel composition: The qualitative part of the composition determination is made by GC-MS. Then, some internal standards are injected with the pure fuel to quantify the proportion of each compound of the fuel using the De Saint Laumer [2] method to conclude on an accurate composition.

2.Experiments:
For this, an experimental pilot (see illustration) was set up in order to be able to make oxidation and pyrolysis between 600°C and 1000°C, a residence time between 0.5s and 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 determined, 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 modify the mechanism accordingly. Once the mechanism is generated, it will be possible to use it for different operating conditions closer to those encountered in ramjets

Illustration : description of the experimental setup



Main results

The thesis started in December 2021 and very few results have been obtained so far

On the other hand, most of the results related to this work are confidential

References :

[1] « PSS-Onera-2020-v2.pdf ». Consulté le: 3 mai 2022. [En ligne]. Disponible sur: https://www.onera.fr/sites/default/files/branche/PSS-Onera-2020-v2.pdf

[2] J.-Y. de Saint Laumer, E. Cicchetti, P. Merle, J. Egger, et A. Chaintreau, « Quantification in Gas Chromatography: Prediction of Flame Ionization Detector Response Factors from Combustion Enthalpies and Molecular Structures », *Anal. Chem.*, vol. 82, n° 15, p. 6457-6462, août 2010

2022

Research subject : Development of thermodynamic model, algorithms and computational tools to assess the energy transformations of reactive working fluids in thermodynamic cycles.

Konstantin SAMUKOV (1 year)

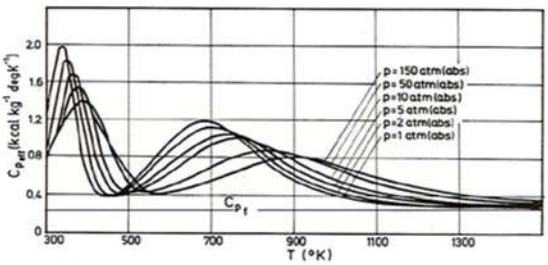
Romain PRIVAT, Silvia LASALA

Keywords : Reactive fluids, thermodynamics, thermal energy conversion

General context, scientific issues :

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

Illustration : Heat capacity of the N_2O_4 dissociating system [1]



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 :

Calculation tool will be entirely coded in Fortran, and will require the preliminary selection, improvement and implementation of: (1) a predictive equation of state based on the group contribution method; (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 fictitious 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. Finally, this research will be focused on the spectroscopy analysis of reactive fluids that will be tested at LRGP in the context of the ERC-REACHER project

Main results

The PhD thesis has just started, a few amount of work has been done.
Reactive fluids were highly investigated in the Soviet Union in the 1960-1980s [2], the results of their researches were gathered and analyzed.

Simple subroutines that are going to be used in computational tools have been written in Fortran

References :

1] Krasin AK, Nesterenko VB. Dissociating gases: a new class of coolants and working substances for large power plants. At Energy Rev 1971;9:177.

[2] Vesci Acad Navuk BSSR 1965-1989.

PRODUCT ENGINEERING

LRGP
LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

2022

Research subject : : Nanoengineered graphitic carbon nitride for multicatalytic hydrogen production

Bolatov Asset (Post-Doc)

Raphaël Schneider, Bolat Uralbekov

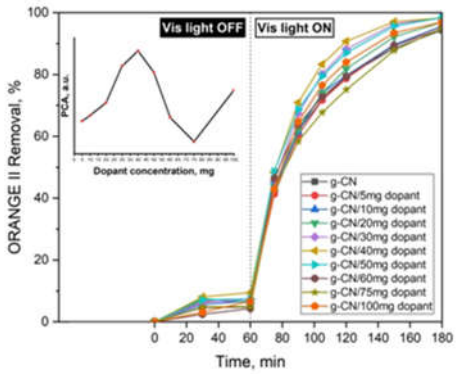
Axe PRODUCT ENGINEERING

Keywords : Graphitic carbon nitride, photocatalysis, multicatalytic hydrogen production, semiconductor photocatalyst, porous 3-D g-CN synthesis and functionalization

General context, scientific issues :

The production of hydrogen (H_2) and the use of its environmentally friendly alternative fuel is one of the most important needs of modern science and society as a whole [1].
As it is known, H_2 can be produced by steam reforming, photoelectrolysis, etc. However, there are some limitations in the use of these processes (CO_2 emissions, their cost and the need to use renewable energy sources) [2].
In this context, the development and improvement of catalysts based on semiconductors for photocatalysis, including H_2 production via water splitting, is the most affordable solution [3].

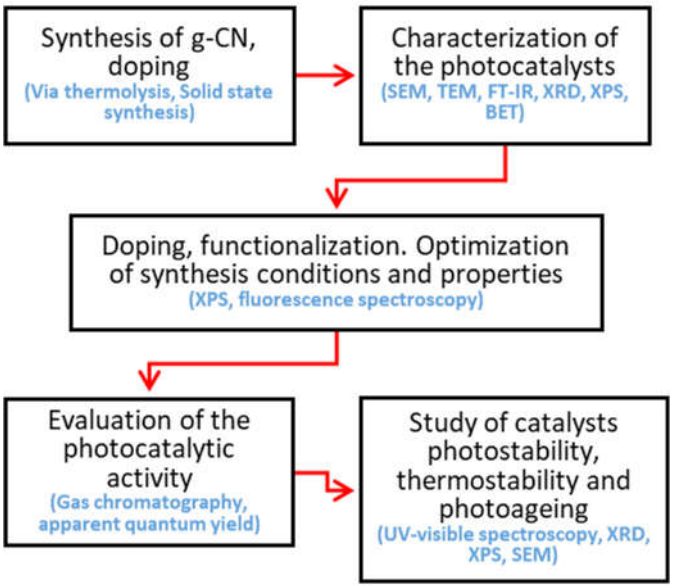
Illustration : Influence of F-doping on the photocatalytic activity of g-CN in degradation reactions.



Objectives and stakes :

Development of an efficient, scalable and economical approach for the synthesis of functionalized g-CN to boost photocatalytic reactions.
– Synthesis of porous 3-D g-CN and doping/functionalization.
– Theoretical calculations and ESR measurements.
– Photocatalytic and thermophotocatalytic H_2 production.
–Investigation of the stability and the reuse of the catalysts.

Methodology :



Main results

At this stage of the study, g-CN was synthesized by a stepwise solid-state reaction from urea. To prepare catalysts, the g-CN compound was doped with fluoride ions during a hydrothermal synthesis.
Successful preparation of the catalysts was confirmed by FT-IR. All samples had similar spectra, which confirmed that the g-CN structure was not damaged after doping with fluorine.
UV–Vis DRS curves for various g-CN-based catalysts reflects that doping with fluorine leads to a blue shift of g-CN absorption.
As shown in the figure, photocatalytic efficiencies under visible light irradiation toward Orange II degradation were gradually enhanced with the increase of the dopant percentage (the greatest Orange II removal was 91% after 1 hour of irradiation when the dopant amount is 8%) and then slowly decreased. These changes in the photocatalytic activity originate from changes in the electrons distributions, from a downshift of the energy levels of g-CN and from the decreased hole-electron recombination that allow the production of a higher amount of reactive oxygen species [4].

References :

[1] J. Jia et al., Nat. Commun. 2016, 7, 13237.
[2] A. Hakki et al., Encyclopedia of Interfacial Chem., Surface Science and Electrochemistry, 2018, 413-419.
[3] S. Chen et al., Nat. Rev. Mater. 2017, 2, 17050.
[4] Y. Tan et al., Applied Catalysis B: Environmental, 2022, 121133

2022

Research subject : Effect Of The Incorporation Of Silica Nanoparticles On The Stability And Rheological Behavior Of Xanthan Gum Formulations For Use In Enhanced Oil Recovery

Dayan Lizeth Buitrago Rincon (3rd year)

Cécile Lemaitre , Veronique Sadtler

Axe PRODUCT ENGINEERING

Keywords : Xanthan gum, Silica nanoparticles, Rheological behavior, Nanofluids, Dispersion processes

General context, scientific issues :

Colloidal suspensions containing xanthan gum (XG) have been widely used as a thickener and gelling agent for different uses in petroleum, food, cosmetics and other multiple industries [1]. In many of these applications, brines are used as solvents. However, the changes in conformational structure of the xanthan gum macromolecules in a buffered ionic solution such as NaCl directly impact the rheological and stabilized behavior of polymeric aqueous solutions [2]. Therefore, hydrophilic silica nanoparticles (NpSiO2) is proposed, to improve the rheological behavior of these polymer solutions by increasing their viscosity in monovalent ion environments [2,3].

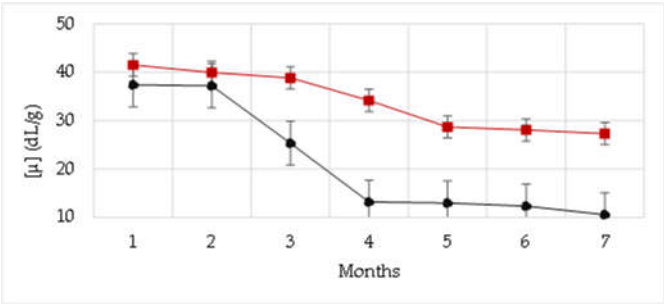
Objectives and stakes :

Evaluate the effect of the incorporation of hydrophilic silica nanoparticles (NpSiO2) on the rheological behavior of XG polymer solutions in different monovalent ion (NaCl) environments.

Methodology :

The effect of silica nanoparticles (NP-SiO2) in xanthan gum (XG) solutions was investigated through the analysis of viscosity profiles. First, hydrocolloid XG solutions and hydrophilic NP-SiO2 suspensions were characterized individually through rheological measurements, with and without salt (NaCl). Then, nanofluids composed of XG and NP-SiO2 dispersed in water and brine were studied through two different aging tests. The addition of nanoparticles was shown to produce a slight effect on the viscosity of the fresh fluids (initial time), while a more remarka-ble effect was observed over time. In particular, it appears that the presence of NP-SiO2 stabiliz-es the polymer solution by maintaining its viscosity level in time, due to a delay in the move-ment of the molecule. Finally, characterization techniques such as confocal microscopy, capillary rheometry, and Zeta potential were implemented to analyze the XG/NP-SiO2 interaction. Intrinsic viscosity and relative viscosity were calculated to understand the molecular interactions.

Illustration : : Intrinsic viscosity [µ] as a function of time. Storage and tests performed at T=60 °C. Nanofluid (–■). Polymer solution (–●).



Main results

The individual components were first characterized in water and brine. XG molecules are satisfyingly dissolved after 24 h and the resulting solutions (without particles) exhibits a shear-thinning behavior. The addition of salt to these solutions causes a viscosity decrease while maintaining a shear-thinning behavior. Nanoparticle suspensions (without polymer) are Newtonian for the considered particle concentrations and their viscosity is not affected by the addition of salt.

The rheology of the XG solutions with and without NP-SiO_2 was characterized over time. The presence of nanoparticles led to higher viscosities. The viscosity of all fluids decreased in time, but the decrease was limited by the presence of nanoparticles, which demonstrates the stabilization of xanthan gum solutions by the addition of nanoparticles. However, these positive effects of NP-SiO_2 are attenuated by the presence of salt.

The intrinsic viscosity of the polymer solutions with and without nanoparticles was calculated from the rheological measurements. The intrinsic viscosity is higher with NP-SiO_2 at every time. This indicates that the hydrodynamics radius of the polymer is larger when nanoparticles are present, which is a sign of polymer/particle interaction.Confocal microscopy images show that the nanoparticles dispersed in water form large aggregates (20 microns), but that the aggregates are much smaller (under 300 nm) in the presence of xanthan gum, evidencing an action of polymer on particle dispersion. It was also shown experimentally that the presence of nanoparticles affects the Zeta potential of XG solutions

References :

[1] Whitcomb P. J., b. J. Ek , Macosko W. (1977). Rheology of Xanthan Gum Solutions. University of Minnesota, Minneapolis.

[2] Pi G., Li Y., Bao M., Mao L., Gong H., Wang Z. (2016). Novel and Environmentally Friendly Oil Spill Dispersant Based on the Synergy of Biopolymer Xanthan Gum and Silica Nanoparticles. Ocean University of China

[3] Min- Ho Oh, Jae-Hyun So, Seung Yang, (1999). Rheological Evidence for the Silica-Mediated Gelation of Xanthan Gum. Journal of Colloid and Interface Science 216, 320 –328

2022

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

Alaric Catard (1st year)

Sandrine Hoppe, Isabelle Chevalot

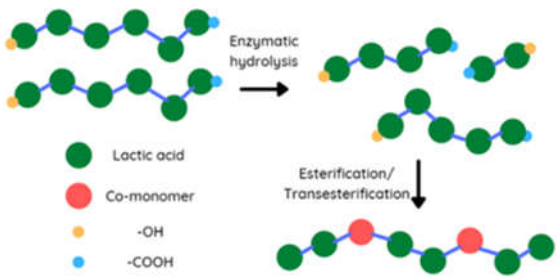
Axe PRODUCT ENGINEERING

Keywords : polylactic acid, enzymes, green solvents, hydrolysis, *Candida antarctica* lipase B, proteinase K, transesterification

General context, scientific issues :

Currently, the vast majority of the plastics used are oil-based and it raises several issues: pollution from oil industries, oil resources depletion… Last decades have seen the emergence of biobased plastics, such as polylactic acid (PLA) to decrease the environmental impacts of plastics. At the end of its life, PLA may be chemically recycled by total depolymerization into its monomers and repolymerization of them enabling « infinite recycling ». However, depolymerization into oligomers may be more energy-friendly.

Illustration : Reaction scheme for obtention of new polymer from PLLA



Objectives and stakes :

This work will focus on partial enzymatic hydrolysis of PLLA (poly L-lactic acid) as a first step, using the following commercial enzymes: a protease (proteinase K) and a lipase (CALB). The activity of these enzymes is different according to the isomers of PLA : proteases are efficient against PLLA unlike lipases which are efficient against PDLA (poly D-lactic acid) [1]. However, some authors reported that lipases can depolymerize PLLA in organic solvents [2]. This study aims to explore "green solvents" with low toxicity to solubilize PLLA making it more accessible to enzymes. As a second step, other enzymes will be produced and their hydrolysis rates will be compared with former enzymes. Finally, as a third step, the objective is to improve different properties of PLLA by enzymatic copolymerization of its oligomers. Enzymatic copolymerization of high molecular weight polymer from oligomers is still challenging.

Methodology :

This study is divided into different parts:
1 - Solubility tests of PLLA in mixtures of green solvents: dimethyl carbonate (DMC)/diethyl carbonate (DEC) with buffer and acetone. 2 - Tests of enzymatic hydrolysis of PLLA (using proteinase K and CALB) in these solvents and buffers to check impact of PLA's dissolution on hydrolysis. Other parameters (temperature, crystallinity…) are investigated. 3 - Screening of other enzymes (cutinases and proteases) which are able to hydrolyze PLLA and try to obtain better hydrolysis performance than those obtained with former enzymes. 4 - Finding of molecules to co-polymerize with PLLA by enzymatic transesterification to obtain better properties.

Main results

- Solubility tests of PLLA in mixtures of DMC/DEC – acetone – buffer:

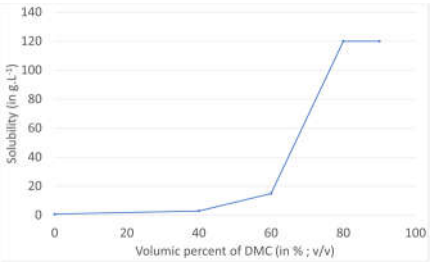


Figure 1. Solubility of PLLA in mixtures of DMC-acetone-buffer at 85°C (with 10% (v/v) of buffer in each samples)

PLLA reaches the highest solubility (120 $g.L^{-1}$) in the mixture of DMC-Buffer 90/10 (v/v) (volume fraction of buffer is kept constant between all samples).

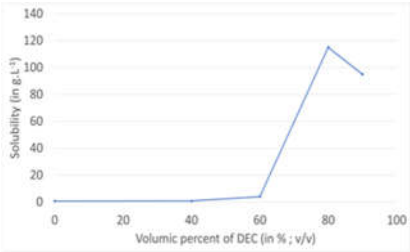


Figure 2. Solubility of PLLA in mixtures of DEC-acetone-buffer at 115°C (with 10% (v/v) of buffer in each samples

PLLA reaches the highest solubility (115 $g.L^{-1}$) in the mixture of DEC -Acetone-Buffer 80/10/10 (v/v) (volume fraction of buffer is kept constant between all samples).

References :

[1] Kawai F, Nakadai K, Nishioka E, Nakajima H, Ohara H, Masaki K, et al. Different enantioselectivity of two types of poly(lactic acid) depolymerases toward poly(l-lactic acid) and poly(d-lactic acid). Polymer Degradation and Stability. 2011;96(7):1342–8.
[2] Takahashi Y, Okajima S, Toshima K, Matsumura S. Lipase-Catalyzed Transformation of Poly(lactic acid) into Cyclic Oligomers. Macromol Biosci. 2004;4(3):346–53

2022

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

Bilel CHOUCHENE

Raphaël SCHNEIDER

Axe PRODUCT ENGINEERING

Keywords : Quantum dots (QDs), Photoluminescence, QDs/photopolymer composites, lighting devices

General context, scientific issues :

Luminescent nanoparticles (NPs) have been widely used in research and application fields due to their distinctive properties, especially in the field of light-emitting diodes **[1,2]**. However, there is an urgent demand to improve their luminescence efficiency, which is greatly reduced by surface effects. In this context, our work is based on the development of the synthesis of non-toxic and cheap NPs/polymer nanocomposite with characteristics combining the properties of NPs and coating polymers for applications in the field of micro- and nano-manufacturing.

Objectives and stakes :

The overall objective of this work is to develop innovative photoluminescent textiles by coating them with an advanced composite film combining heavy metal-free and non-toxic quantum dots (QDs) with a biocompatible formulation of light-cured methacrylate for a new generation of photoluminescent textiles

Methodology :

To achieve the objective previously described, the following methodology will be implemented:

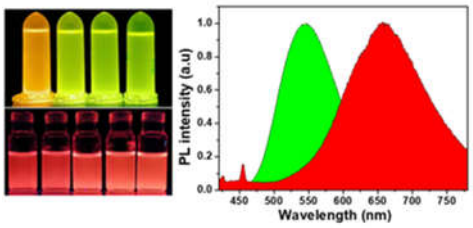
1- Synthesis of silver- or copper-based QDs with tunable optical properties in the visible range.

2- Structural and optical characterizations of synthesized QDs, and study of their photostability

3- Developing a photo-induced synthesis of highly photoluminescent QDs/polymer nanoassemblies by adjusting the size, composition, organization/spatial distribution of QDs in the polymer film and implementing this technology in textile applications

4- Preparing new photoluminescent textiles with targeted photometric characteristics when combined with violet/blue LEDs chips.

Illustration : Digital photograph of green and red QDs prepared and the corresponding PL emission spectra



Main results

During the first quarter of work:

Orange, yellow and green-emitting Cu- or Ag-based QDs will be prepared by a thermal-induced decomposition of precursors in presence of a mixture of dodecanethiol (DDT) used as ligand and 1-octadecene (ODE).

The crystal structure and phase of the as prepared QDs were analyzed via X-ray powder diffraction (XRD). The results revealed that the prepared particles crystallize in the cubic form of ZnS (PDF n° 05-0566) [3].

Photostability tests of the synthesized QDs have been carried out and show that the dots are photostable under UV irradiation at 405 nm.

The prepared particles show high photoluminescence properties with quantum yields varying between 45 and 63%.

References :

[1] X. Wang, X. Yan, W. Li, K. Sun, Adv. Mater. 24 (2012) 2742–2747.

[2] Z. Xia, C. Ma, M.S. Molokeev, Q. Liu, K. Rickert, K.R. Poeppelmeier, J. Am. Chem. Soc. 137 (2015) 12494–12497

[3] J. Song, C. Ma, W. Zhang, X. Li, W. Zhang, R. Wu, X. Cheng, A. Ali, M. Yang, L. Zhu, R. Xia, X. Xu, ACS Appl. Mater. Interfaces 8 (2016) 24826-24836.

2022

Research subject : Development and design of new hybrid materials such as MOFs with advanced functionalities for photocatalysis applied to water treatment.

Ola Haidar (1st year)

Thibault Roques Carmes (LRGP), Joumana Toufaily (LEADDER-Lebanon),

Mohamad Hmadeh (AUB-Lebanon)

Axe PRODUCT ENGINEERING

Keywords : Photocatalytic degradation-Emerging contaminants-Metal organic framewroks-UiO-66.

General context, scientific issues :

Emerging contaminants (EOCs) in water, such as pharmaceuticals and personal care products (PPCPs), industrial chemicals, antiseptic and antimicrobial agents, flame retardants, detergents and their derivatives, plasticizers and their derivatives, are of growing environmental concern and there is a need to develop new materials and technologies for their efficient removal from water[1]. Photocatalysis process is a promising technology for environmental remediation. In the continuous search of new heterogeneous photocatalysts, metal-organic frameworks (MOFs) have recently emerged as a new type of photoactive materials for water remediation[2].Metal organic frameworks (MOFs) are a novel class of crystalline materials based on the coordination of metal clusters by organic linkers. These materials are known for their ultrahigh porosity, high surface area (up to 12000 m2/g), flexibility, chemical tunability and

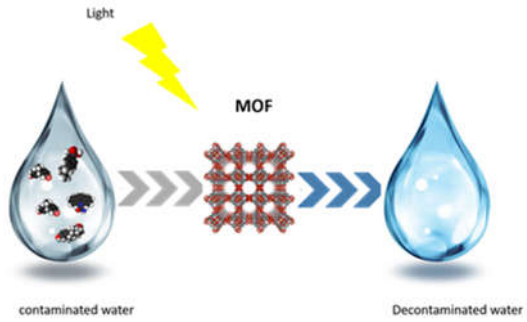
Objectives and stakes :

In this project, we aim to use Zirconium-based MOFs, namely UiO-66, as photocatalyst for the removal of Emerging contaminants from water.
We report the solvothermal synthesis of various functionalized, defective, and doped UiO-66 derivatives by combining different type of modulators, organic linkers, and metal salt.
Ten UiO-66 MOFs based structures were fully characterized using SEM/EDX, TGA and BET.

Methodology :

1-Synthesis and characterization of UiO-66(Zr) rigid structures.
2-Photocatalytic degradation tests with model pollutants such as:Carbamezepine, Ibuprofen, Metolachlor, Bisphenol A, Propranolol hydrochloride, 2-Naphthol, 1-Naphthyl amine and 2,4-Dichlorophenol.
3- Evaluation of MOF structures to degrade a cocktail of micropollutants from real river water in Meurthe (France).

Illustration : Photocatalytic degradation of ECs using MOFs.



Main results

A series of defective, doped, and functionalized Zr-based MOFs have been synthesized via solvothermal means, fully characterized via scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), BET analysis, and thermogravimetric analysis (TGA).
These MOFs are ready now to be tested for the removal of organic pollutants from water.
This study will help us determine the best functional groups, level of defects, and metal combination to enhance MOF's catalysis properties. It is anticipated that this work will pave the way for the development of new and highly efficient MOF catalyst for water remediation.

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2022

Research subject : Powders flowability and dustiness behavior: an attempt to predict safety issues

Maria Camila Jiménez Garavito (3rd year)

Graciela Cares Pacheco Véronique Falk, Fabien Gerardin

Axe PRODUCT ENGINEERING | INRS

Keywords : powder, flowability, characterization, dustiness, safety, nanoparticles, risks, dust exposure.

General context, scientific issues :

Powders are part of the conception and final products of different industries such as construction, pharmaceuticals, food, and cosmetics. At least 60% of chemical products are in powder form, with approximately 200,000 employees in France in charge of its process. Powder handling is a major topic as many complications arise during manufacturing and transport. The flowability of powders and/or dust generation during unit operations are key points, leading to safety problems for the employees. In order to ensure manufacturing, flowability issues can be overcome by: the modification of facilities that are seldom universal; the fluidization of powders, which then involves a separation operation increasing process complexity; the addition of nanoparticles (NP), or glidants, because it is cost/benefit effective. Glidants adhere to the powder particles decreasing interparticle forces or absorbing moisture, eliminating liquid bridges between particles. Nevertheless, the use of glidants could lead to health and environmental implications and dust generation, which increases employee exposure. The health, safety, and environmental hazard of nanoparticles are not yet well known, even if recent studies have shown their cytotoxicity [1].

Consequently, understanding end-use properties such as powders' flowability and dustiness could lead to new and

Objectives and stakes :

- Establish a link between flowability and dustiness.
- Increase the understanding of the dustiness phenomenon.
- Develop guidelines for safe handling: decreasing dust exposure and ingredients/additives choice.

Methodology :

1. Define the influential factors on powder flowability by experimental design (DoE).
2. To determine how flowability enhancement impacts dust generation.
3. Develop methodologies for choosing ingredients to anticipate formulation and process changes, thus reducing employees' exposure to risks

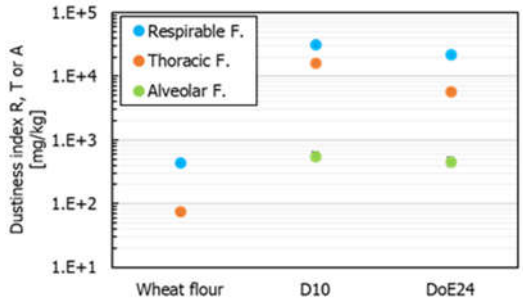

Fig1. Rotating drum dustiness measure of pure wheat flour, D10 glidant, and the mixture of both (DoE24)

Main results

Powders flow enhancement with glidants was studied with a D-optimal experimental design (DoE). The main objective was to identify the action mechanisms of NP on granular flows [2]. Several factors were chosen (powders, glidants, moisture conditioning, surface coverage, and protocol) and related to friction, cohesion, and flow behavior using Mohr-Coulomb yield criterion parameters and Hausner ratio as a flow index in the quasi-static regime (QSR). The DoE analysis showed that powders' flow behavior is highly dependent on the type of powder due to grain properties, limiting global observations. Regarding the mechanisms of action, we show that bulk friction does not play a role in granular flows in the quasit-static regime, varying randomly between the DoE runs. NP acts as surface modifiers, increasing powders' flowability by reducing adhesive forces through surface energy changes or acting as separators.

The dustiness of the mixtures having the best flow behavior was determined using a rotating drum (RD) and vortex shaker (VS). The results showed that powders covered with 40% of glidants generated a similar amount of dust in all inhalable fractions than glidants alone. We conclude that dustiness increases when the flowability is improved by glidants (Fig 1).
We propose a protocol for adding NP's required amount based on powder's surface coverage. This method may reduce the amount of NP in formulations to mitigate the risks of exposure.

References :

[1] M. Ricaud et O. Witschger, Les nanomatériaux - Brochure - INRS 2012.
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2022

Research subject : Scaling control by the use of ultrasonic guided waves associated with the heterodyne effect of multiple frequencies

Nihad KAMAR (3rd year)

Hervé MUHR, Marie LE PAGE MOSTEFA

Axe PRODUCT ENGINEERING

Keywords : Scaling; Heat exchanger; Heat transfer; Ultrasonic transducer; Crystallization; Calcium carbonate.

General context, scientific issues :

The objective of this thesis is the implementation of an alternative ecological system to prevent fouling of heat exchangers. This antifouling system uses multiple frequency heterodyne technology based on the combination of ultrasonic passbands (spectrum scanning) combined with guided wave technology. The action of the ultrasounds will consist in preventing the formation of deposits, especially calcium carbonate, on the exchanger plates. This technology concentrates the ultrasounds on the metal surfaces and limits the propagation of these latter in the water.

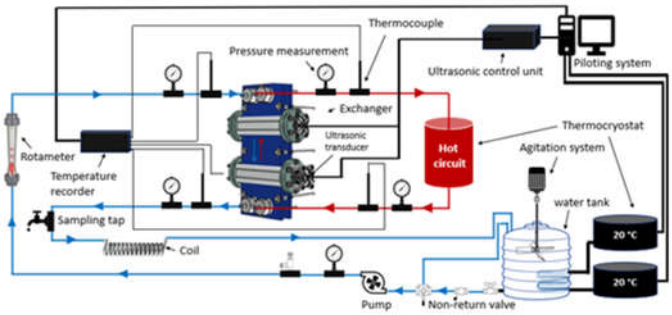
Objectives and stakes :

- Establish the feasibility of limiting fouling by using heterodyne guided waves;
- Optimize the positioning of the transducers;
- Characterize the effective dose, including the minimum power for which there is a significant effect on the limitation of deposit;
- Identify the effect of heterodyne technology on the nature of the deposit.

Methodology :

An experimental device has been designed, developed and implemented. It consists of a pilot size heat exchanger containing 10 plates with an exchange area of 0.38 m2. The exchanger is also equipped with thermocouples in the inlet and outlet streams to determine the heat transfer coefficient. A 100 liters tank of water containing 143 ± 23 mg. L -1 of Ca2+ is pumped into the exchanger and heated from 20 to 50°C. Due to the high content of dissolved calcium carbonate and the decrease of its solubility with increasing temperature [1], calcium carbonate precipitates inside and on the surfaces of the heat exchanger. The deposit is then dissolved in nitric acid and analyzed by ICP-OES to quantify the amount deposited in grams/day/m2. Analyses of the precipitated solid were performed by RAMAN spectroscopy, scanning electron microscopy, 3D and confocal digital microscopy, and laser granulometry, to determine the nature, polymorphism, and size distribution of the precipitated particles.
The ultrasonic device used in this study is placed on the exchanger using a fixation system in the most sensitive area for calcium carbonate formation. This location was identified through a comparison between a numerical model of temperature distribution and fluid flow in the cold channels of the exchanger, and a scan of the scaled plates with a 3D digital microscope. To generate the heterodyne effect, two transducers have been fixed on their resonance frequencies, 45 kHz and 27 kHz.

Illustration : Scheme of the experimental set-up in the presence of the heterodyne effect of multiple frequencies



Main results

The results obtained show that the amount of scale deposited inside the exchanger without ultrasonic treatment is about 4.8 ± 0.9 grams/day/m2 and that the precipitate is composed of calcite agglomerates of 251 µm on average diameter by volume.

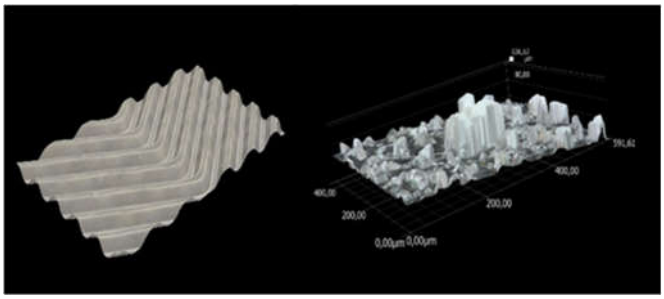


Figure 1. The thickness of the scale at the inlet of the first compartment of the exchanger without any treatment after 72 h of operation, Tf °C (20), Tc °C (50), flow rate 100 L.h -1

The optimized power for the heterodyne effect is 15 VA. It reduces the deposit by 57%, without changing the nature of the deposit

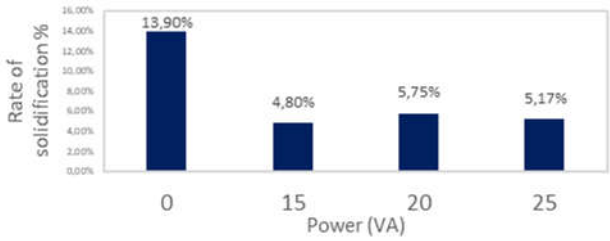


Figure 2. The solidification rate of the deposited quantity in the presence of the heterodyne effect at different ultrasonic power

2022

Research subject : Peptidic hydrolysate of interest simulation by Enzymatic membrane reactor

Kaugarenia Nastassia (3rd year)

Romain Kapel, François Lesage

Axe PRODUCT ENGINEERING

Keywords : Bioactive hydrolysates, Enzymatic proteolysis, Kinetic modeling, Multicriteria optimization, Simulation.

General context, scientific issues :

Protein hydrolysates use in food and pharmaceutics industry gain importance because of their functional or nutritional properties. They are usually produced in a batch reactor by enzymatic hydrolysis. But, that process is expensive due to the development phase and enzyme cost, so its industrial massive employment encounter obstacles [1]. In that case, a strategy with an enzymatic proteolysis process coupled to membrane separation can be applied to overcome these limits.

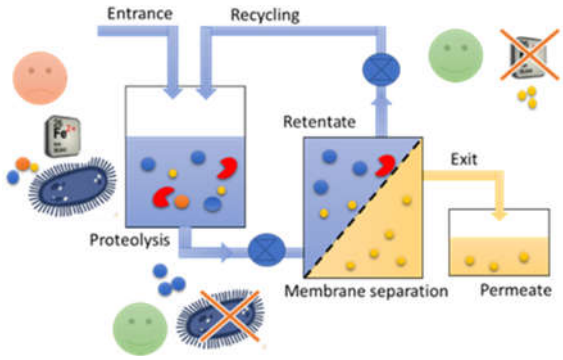
Objectives and stakes :

An EMR (Enzymatic Membrane Reactor) allows to strongly decrease production cost by enzyme recycling and continuous process. Nevertheless, the production of one hydrolysate is hardly manageable, because the mixture could be made up of more than 200 various peptides [2]. To overcome these limitations and enable ingredients development from proteins, the project aims to elaborate a methodology to simulate the hydrolysate composition in EMR process for a duo enzyme/protein: by preliminary enzymatic activity and material balance equations, suitable proteolysis conditions could be known to have a stable hydrolysate production [3]. Finally, the developed approach makes it possible to have a high value functional hydrolysate at reasonable cost with a possibility to scale up with standardization.

Methodology :

First year, a method to monitor a stable hydrolysate was developed. Second year, this methodology was applied to model and optimize a batch production of an hydrolysate with interesting properties. This third year, implementation of proteolysis-ultrafiltration simulation is targeted. To do so, a batch process of proteolysis reaction Prolyve/total Rapeseed proteins was produced and several ultrafiltration (UF) membranes calibrations were made. Molecular cut-off (10-100 kDa), transmembrane pressure (1-2 bar) and shear rate (3000-6000 s-1) were studied to determine retention rate (R) and characterize the selectivity for each set of parameters. Then, UF mass balance equations were applied to predict proteins and peptides fractioning performances in retentate and permeate compartments in concentration (FRV) and diafiltration (DV) mode

Illustration : Optimal production of hydrolysate with antimicrobial function and chelating properties



Main results

The most optimal separation predictions were validated experimentally, characterized by a retention close to 1 for proteins and an efficient transmission of peptides, with a high permeate flux. Thus, a cut-off threshold of 50 kDa, a PTM of 2 bars and a shear rate of 3000 s-1 were chosen and implemented in discontinuous concentration mode up to reduction factor of 10. On the retentate side, the purity in proteins of 63.5% and the yield of napins of 1.2 were obtained experimentally, at FRV 10, i.e. an average difference of 8.5% and 20%, respectively with the simulated values. On the permeate side, the yield of experimental total peptides at FRV 10 of 0.46 was obtained, corresponding to a difference of 8.5% with the prediction. In DV mode, the comparison of the experimental values to the simulations was also good for the retentate side except for the yield of total peptides which showed greater difference (36.6%). The transmission of total peptides in the permeate appeared stabilized for peptides below 500 Da beyond the 4th diavolume, whereas these peptides were still present in the retentate. Concerning the other peptide fractions, an overvaluation of the transmission by the simulation was observed, with a less efficient transmission experimentally. Further investigations are necessary to be able to understand the differences.

References :

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[2] A. Trusek-Holownia, et al., Chem. Eng. J., v. 305, p. 61–68. 2016

[3] A. Bodin, et al., J. Chrom. B, v. 1006, p. 71–79. 2015

2022

Research subject : Multi-material structures with damping zones spatially controlled by 3D printing

Alejandra Lara García (3nd year)

Cécile Nouvel, Hakim Boudaoud (ERPI EA 6737), Sandrine Hoppe

Axe PRODUCT ENGINEERING

Keywords : 3D Printing, FDM, interfacial adhesion, thermoplastic, thermoplastic elastomer

General context, scientific issues :

Additive manufacturing, or 3D printing, have shown to have many important applications nowadays. The fused filament fabrication (FFF) is one of the most used technologies of 3D printing. Among its advantages, it allows to obtain extremely complex and personalized objects, which would be impossible to obtain using another manufacturing process. Nowadays, a large range of thermoplastic polymers are available for FFF process. Moreover, there are some multi-material objects printed by FFF but they suffer of interlayer affinity especially when printed objects are made from different polymers (i.e. polymers with different affinities). Even though this adhesion problem exists in all polymer manufacturing process, it has been poorly addressed in the 3D printing world.

Objectives and stakes :

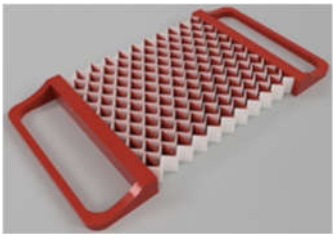
This thesis aims to synthesize and elaborate a 3D printable thermoplastic elastomer (TPE) filament presenting a good affinity to poly (lactic acid) (PLA). This filament will be formulated as a TPE, which will include a PLA as soft block and a classic rigid block, poly (butylene terephthalate) (PBT). Our goal is to be able to allow the fabrication of 3D printed objects including rigid and soft parts (fig. 1)

The goal is the fabrication of multi-material structures with spatially controlled damping properties thanks to an optimal distribution between soft (TPE) and rigid (PLA) areas (Fig. 1). Such damping structures could be designed in the future to attenuate mechanical and acoustic vibratory phenomena or to have shape memory type behaviours. So far, in the literature, studies concerning multi-material polymer parts combining TPE and TP are very few, as well as studies concerning their interfacial affinity. Finally, there is no TPE filament that has a good affinity with PLA

Methodology :

1) Synthesis and characterization of new TPE including a soft polyester block by reactive extrusion.
2) Formulation of TPE filaments:
-Formulation of a new TPE, fabrication, quality control and printability of filament
-Formulation of commercial TPE, and improvement of interfacial adhesion with PLA
-Characterization of interfacial properties between the new filaments and a PLA filament.
3) Optimization of mechanical properties of printed objects :
-Evaluation of vibratory properties (i.e. damping properties)
-Optimization of distribution between flexible and rigid zones

Illustration : Example of multi-material object including PLA, as rigid part, in red; and TPE, as soft part, in white.



Main results

Our research is focused on the synthesis by reactive extrusion of a new TPE incorporating PLA as soft block and PBT as rigid block. For this, a screening was done using low quantities of material and titanium butoxide (TBT) as catalyst to aid the reaction [2]. Varying the ratio PBT/PLA and the reaction time, a micro-compounder as internal mixer (analogue to an extruder) was used to create samples. Characterization such as hardness, FTIR, modulated DSC, DMTA and 1H and C13 NMR demonstrated the possible transesterification reaction between PLA /PBT resulting in multi-block copolymers.[1] In parallel, tests were carried out in order to transpose some operating conditions carried out on a small scale to a pilot scale (with an extruder). In addition, other essays are being done using an amorphous PLA to promote transesterification reactions between PLA and PBT, as well we plan to expand our research using a LMW PLA.
In parallel, a new formulated TPE filament was successfully extruded, based on a commercial TPE with four different biomass additives, as adhesion promoters, in order to test the adhesion of TPE/PLA. Filaments with no defects, such as bubbles, were obtained. All but one of the additives gave acceptable results in terms of hardness and MFI. Except for this formulation, all filaments were printable. An improvement of the interfacial adhesion was obtained, especially with one additive that showed the greatest enhancement. In order to attaint our last objective, some mechanical properties will be measured. These entails vibratory properties (using a vibration system) and damping properties (using DMA in temperature sweep and frequency sweep).Finally, we will begin the 4D printing of large structures with tailored mechanical properties, with PLA and in TPE (pure and formulated) (Fig. 1) [2].

References :

[1] I. Irska *et al.*, "Poly(butylene terephthalate)/polylactic acid based copolyesters and blends: miscibility-structure-property relationship," *Express Polym. Lett.*, vol. 14, no. 1, pp. 26–47, 2020.

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2022

Research subject : subject : Colloidal synthesis, optical and structural properties of ternary doped ZnSeS quantum dots

Salima MABROUK (4th year)

Raphaël SCHNEIDER, Rafik BENCHAABANE

Axe PRODUCT ENGINEERING

Keywords : Ternary ZnSeS QDs, Cu-doped QDs, Pb2+ detection, fluorescence, dynamic quenching, sensors.

General context, scientific issues :

Ternary alloyed QD nanocrystals offer better flexibility in bandgap modulation and composition control than binary QDs, which provide them with advantages in device applications [1]. Generally, alloyed QDs have been reported to generate greater output efficiency than conventional QD systems [2]. Hence, there is a growing interest in the study and development of alloyed QD nanocrystals. We have focused our research attention on the study of ternary alloyed ZnSeS/ZnS core/shell QDs doped with Cu2+ ions. These QDs are prepared via a simple aqueous synthetic route and have a pure Cu-related photoluminescence located at 500 nm and a PL quantum yield of 20%. The PL emission of these QDs was demonstrated to be selectively quenched by Pb2+ ions and a method for the rapid and sensitive detection of Pb2+ in real water samples was developed.

Objectives and stakes :

Our objectives are:
(i) Study the doping of these nanocrystals by Cu2+ ions (optimization of experimental parameters to obtain a good crystallinity, a small dispersion in size and an excellent stability in solution and in the solid state).
(ii) Evaluate the impact of increasing the concentration of Pb2+ ions on the PL intensity of these QDs.
(iii) Study the effects of the ZnS shell on the detection of Pb2+ ions.
(iv) Study the quenching mechanism using on PL lifetime measurements and UV-visible absorption.

Methodology :

The synthesis of Cu-doped ZnSeS/ZnS/ZnS core/shell QDs capped with 3-MPA ligand is described using Zn (NO3)2, NaHSe and Na2S (Fig. 1). The pH was adjusted to 11 and the solution was heated to 100°C. After 4 h of growth, a Cu-doped ZnS and a ZnS shells were installed at the periphery of the ZnSeS core. The prepared Cu-doped ZnSeS/ZnS QDs were characterized by UV-visible absorption, PL spectroscopy, X-ray diffraction (XRD) and MET.

A rapid and simple method was developed for the detection of Pb2+ ions in real water using ZnSeS/Cu:ZnS/ZnS QDs

Figure 1. Schematic representation of the synthesis of ZnSeS/Cu:ZnS/ZnS QDs.

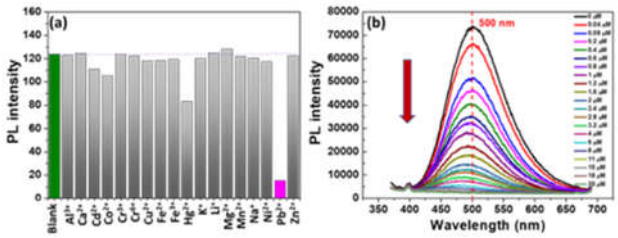


Figure 2. (a) Sensitivity of ZnSeS/Cu:ZnS/ZnS QDs towards various metal cations (b) PL emission spectra of ZnSeS/Cu:ZnS/ZnS QDs dispersed in water upon addition of various concentrations of Pb^{2+}.

Main results

• After two shell growth, a significant increase of the PL intensity and so the PL QY, was observed thanks to the effective elimination of the surface defects of ZnSeS QDs by the epitaxial growth of the ZnS shell.
•The Cu-related PL emission of ZnSeS/Cu:ZnS/ZnS nanocrystals is located at 500 nm and their PL QY is of 20%.
•ZnSeS/Cu:ZnS/ZnS QDs were used as photo-luminescent probes for the detection of Pb2+ and a selective quenching of the PL emission in the presence of Pb2+ was observed (Fig.2a).
•The fast response and the high sensitivity of ZnSeS/Cu:ZnS/ZnS QDs towards Pb2+ combined with the low interference effect of other metal cations make these photoluminescent probes of high interest for Pb2+ sensing in the environment.

References :

[1] C. Ünlü, G.Ü. Tosun, S. Sevim, S. Özçelik, J. Mater. Chem. C 1 (2013) 3026–3034

[2]] W. Ma, J.M. Luther, H. Zheng, Y. Wu, A.P. Alivisatos, Nano Lett. 9

2022

Research subject : Synthesis ,characterization and photocatalytic properties of silver doped zinc oxide

Mouna IBN MAHRSI (2nd year)

Raphaël SCHNEIDER, Fadhila AYARI

Axe PRODUCT ENGINEERING

Keywords : : zinc oxide nanoparticles, Ag-doped ZnO, solar photocatalysis, contaminants.

General context, scientific issues :

There is a growing interest in the study and development of new ZnO-based photocatalysts [1]. We have focused our research attention on the use of silver nanoparticles as modifiers of ZnO with the aim of improve its photocatalytic activity under both UV and visible light for the degradation of organic contaminants. Indeed, modification of semiconductors with noble metals has attracted significant attention as the latter enhance oxidation processes and thus the photocatalytic degradation [2]. Ag-doped ZnO catalysts were succesfully prepared at 300°C via a simple and rapid solvothermal method.

Objectives and stakes :

Our objectives are:
(i) Design of new photocatalytic systems by functionalizing ZnO nanoparticles with Ag(0).
(ii) Analyse the effect of processing parameters on the degradation of organic contaminants.
(iii) Evaluate the performance of the new materials for photocatalytic water remediation under solar light irradiation.
(iv) Evaluate the effect of the Ag doping on the structural and optical properties.
(v) Study the effects of pollutant concentration, catalyst mass, irradiation intensity, pH and doping percentage on the photacatalytic activity.
(vi) Evaluate the stability of the photocatalysts.

Methodology :

The synthesis of ZnO and Ag(0)-ZnO was conducted using Zn (NO3)2, Ag(NO3) and triethanolamine (TEA) in water (Figure 1). The mixed solution was transferred into a Teflon-sealed autoclave and was heated at 110 °C for 2 h. The Zn layered double hydroxides (LDHs) and Zn-Ag LDHs were collected by centrifugation, washed four times with water and dried at 60°C overnight. Finally the obtained products were calcinated at 300°C for 5 min.
The materials were characterized by FT-IR, SEM, TEM, BET, XRD, XPS, Raman spectroscopy and UV-visible absorption.
The photocatalytic performance of undoped and Ag-doped ZnO was evaluated for the degradation of organic contaminants in water.

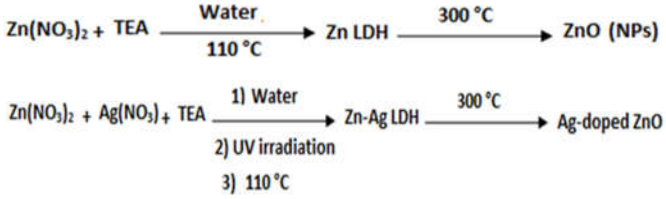


Figure 1. Schematic representation of the synthesis of ZnO and Ag-doped ZnO .

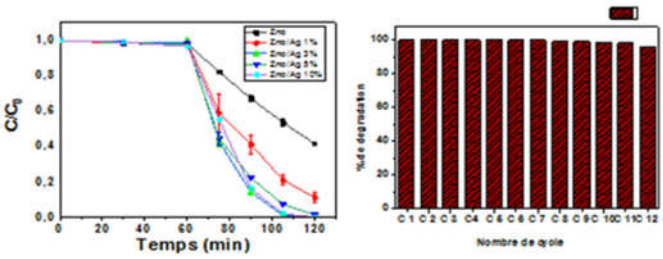


Figure 2. (a) Influence of the Ag loading on the photocatalytic degradation of Rhodamine B, (b) Recyclability of the Ag-doped ZnO photocatalyst

Main results

- The presence of Ag(0) decreases the energy bandgap of ZnO.
- The photocatalytic degradation of cationic or anionic dyes and of Ciprofloxacine under solar irradiation showed that Ag(0)- ZnOcatalysts exhibit better performance than the undoped sample.
- The degradation of Rhodamine B is complete after 60 min irradiation using Ag(3%)-ZnO (Figure 2a).
- The radical trapping experiments demonstrate that superoxide radicals are the main reactive species involved in the photodegradation.
- The Ag(3%)-ZnO/Ag catalyst exhibits a good stability (Figure 2b) and DRX analyses confirm that the cristallinity of the photocatalyst is not affected after 12 cycles of reuse.

References :

[1] K. M. Lee, C. W. Lai, K. S. Ngai, J. C. Juan, Water Res. 88, (2016) 428-448.
[2] P. Sangpour, F. Hashemi, A.Z. Moshfegh, J. Phys. Chem. C 114 (2010) 13955–13961.

2022

Research subject : Ag-In-Zn-Se QDs-sensitized solar cells (QDSSCs)

Saad MAKHLADI (1st year)

Raphaël SCHNEIDER, Thomas GRIES

Axe PRODUCT ENGINEERING

Keywords : Aqueous synthesis, Quaternary Quantum dots, Photovoltaic cell, Surface functionalization, Optoelectronic properties, Cd-free QDs

General context, scientific issues :

The massive increase of energy demand and its impacts on the environment and life cost are major problems of our society. The development of alternative eco-friendly source of energy is crucial. Quantum dots (QDs) are one of the best candidates for the third-generation of "QD-sensitized solar cells (QDSSCs)" [1]. Indeed, these nanocrystals have attracted a lot of interests in many applications such as laser/LEDs, biomedical imaging, photocatalysis and solar cells due to their broad absorption, high fluorescence quantum yield, multiple exciton generation from single photon and tunable optoelectronic properties depending on their composition and/or size.

Ternary Ag-In-Zn-Se QDs (AIZSe) with a bulk bandgap of 1.2 eV, are suitable to absorb solar irradiation and constitute a promising material for solar cell applications. Their components are less toxic than commonly used QDs that contain heavy metal cations (Pb2+, Cd2+ and Hg2+), or anions (As3-) [2], and these nanocrystals have already proved their application in QDSSCs [2,3]. In this project, we will focus on the aqueous phase synthesis of AIZSe QDs because it is environmentally friendly, simple, cheap and easily up-scalable.

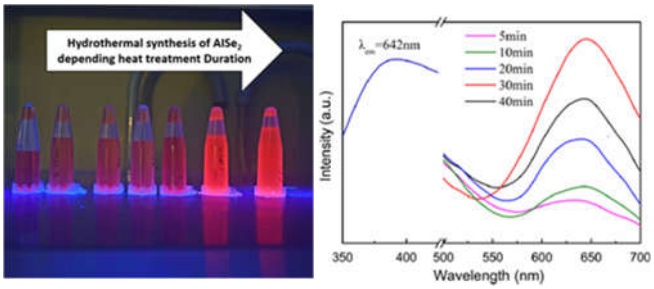
Objectives and stakes :

In the frame of QDSOC project "environmentally friendly colloidal QDs for high performance solar cells", AIZSe QDs will be synthesized using aqueous solution methods. Next, they will be characterized and deposited on TiO2 photoanodes. QDs exhibiting the best performance will be integrated in full QDs-sensitized solar cells with the collaboration of international partners (Belgium, Morocco, South Africa). The ultimate goal is to achieve PCE above 15% which constitute a ground-breaking performance for heavy metals-free PV cells.

Methodology :

QDs will be prepared using an aqueous phase method [4]. Currently, we are optimizing the heat treatment conditions and the surface ligand (such as GSH, 3-MPA, TGA).Next, the molar ratio of Ag/In/Zn/Se will be varied, and the QDs exhibiting the highest performance will be purified and precipitated into powder for further characterization. Later, we will deposit these QDs on porous TiO2 by wet deposition te chniques. TiO2 layers will be prepared and optimized at the IJL lab using different approaches. After the assembly, the QDs photovoltaic performance will be tested

Illustration : (a) Digital photograph of AISe QDs under UV light illumination and (b) the corresponding PL emission spectra.



Main results

Figure (a) shows the results of a hydrothermal preparation of AISe core QDs and Figure (b) the corresponding PL emission spectra which confirm that the annealing time plays a key role on the PL efficiency.

References :

[1] S.Akash et al., Journal of Alloys and Compounds 897 (2022) 162740.
[2] P.-N. Li et al. Journal of Power Sources 354 (2017) 100-107.
[3] T. Kameyama et al, Journal of Physical Chemistry C 118 (2014) 29517–29524.
[4] D. Che et al. Journal of Colloid and Interface Science 463 (2016) 1–7.

2022

Research subject : Rheological study of nuclear glass melts containingPlatinum Group Metal aggregates

Norma Maria PEREIRA MACHADO (4th year)

Philippe MARCHAL, Cécile LEMAITRE, Muriel NEYRET

Axe PRODUCT ENGINEERING | CEA Marcoules

Keywords : Platinum Group Metals (PGM), Thixotropy, Aggregation, Sedimentation, Rheology

General context, scientific issues :

In France, borosilicate glass is used as a matrix to immobilize nuclear fission products resulting from spent fuel reprocessing. In the high-temperature vitrification process (1200 ° C), most of elements to be contained react chemically with the vitrification additives to form a homogeneous glass melt. Platinum Group Metal (PGM) particles are not soluble in the melt and therefore are present as suspended particles of few microns. These particles exhibit an intense aggregation tendency and consequently the suspensions may present an anomalously high apparent viscosity. These systems are characterized by a shear-thinning and a thixotropic behaviors [1].

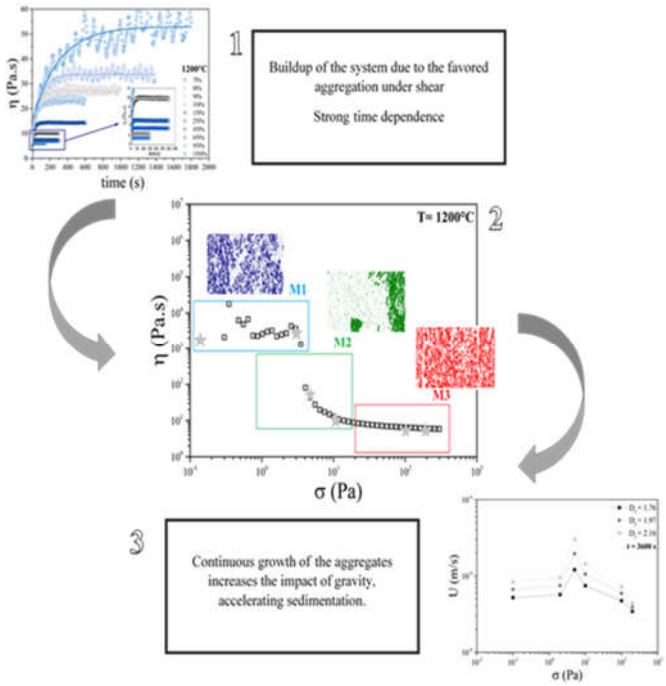
Objectives and stakes :

There are three main objectives to this study:
1. Analysis of the impact of time on the rheological behavior
2. Study of the PGM particles aggregation
3.Linking PGM particles sedimentation to aggregation

Methodology :

The present study aims to provide important inputs for the overall rheological behavior of this system and its features through the characterization of a simulated nuclear glass melt containing 3.0 wt% (1.02 vol%) of PGM particles. A mathematical modeling of the thixotropic behavior of glass melts containing PGM particles is presented for the first time using a model similar to that proposed by Houska (Houska, 1981). This predictive model allow to describe experimental results obtained both in steady state and transient conditions. The impact of the shear stress and time on PGM aggregation degree and sedimentation kinetics is determined using an imposed-stress rheometer at high temperature and imaging analyses via Scanning Electron Microscopy (SEM).

Illustration : Scheme of the thesis in a nutshell: Firstly (1), the thixotropic behavior illustrates the reorganization of the particles with time, which is directly linked with their aggregation (2). The PGM aggregation kinetics is dependent of the imposed shear, gradually changing its size and consequently its settling rate (3).



Main results

The complementary approaches implemented during this thesis have allowed an in-depth understanding of the rheological behavior of glass melts. Thus, this work has brought a qualitative and quantitative interpretation of the observed phenomena allowing a deeper understanding of the material behavior and consequently of the vitrification process. The time dependency of the melt viscosity evidences the reorganization of the particles which affects directly the flow. Hence, the aggregates will gradually increase/ decrease with time, depending on the relative intensities of the forces acting on the particles. Thus, the constant agitation of the samples does not prevent sufficiently the settling of the aggregates, which increases with time. In conclusion, as presented in Figure 1, the three studied phenomena happen simultaneously and are mutually dependent.

References :

[1] C. Hanotin, J. Puig, M. Neyret, P. Marchal, Journal of Nuclear Materials 477 (2016) 102-109

2022

Research subject : Development of PBT-vitrimer composites based on functionalized hollow glass beads

Quentin-Arthur Poutrel (Post-Doc)

Sandrine Hoppe

Axe PRODUCT ENGINEERING

Keywords : Vitrimère, PBT, Composites, Procédés, Transfert technologique

General context, scientific issues :

PBT vitrimer, a partially crosslinked thermoplastic material with reprocessing and recycling properties, have shown outstanding potential for improved mechanical properties with limited change compared to classic PBT. [1,2] Nonetheless, it is yet to prove its industrialisation capabilities either in traditional applications or diversification towards new uses. Hence the project aims to:

(i) Develop those PBT vitrimer matrices and lightweight composites (embedded hollow glass beads) with industrial processes

(ii) Understanding their rheological behaviour in solid and liquid state

(iii) Functionalising glass bead to improve matrix/ reinforcements interface

(iv) Understanding impact of the above functionalisation on rheological behaviour and PBT vitrimer properties

Objectives and stakes :

- Functionalisation of glass bead for PBT vitrimer matrices
- In situ curing of vitrimer compound during PBT extrusion
- Composites development with industrial compatible methods
- Eco-friendly processes for functionalisation
- Lightweight composite properties investigation
- Application and limits of PBT vitrimer (& composites) for industries

Methodology :

- Optimisation to generalise extrusion parameter for polymer and composites
- Manufacture of samples for thermomechanical and rheological testing through microcompounder
- Comparison of properties of model developed at the LEMTA Nancy

Illustration : PBT vitrimer during extrusion and various formulation extruded by kilograms

Main results

Extrusion and compounding of several PBT vitrimer formulation and recycled versions
Extrusion of PBT and PBT vitrimer composites with sample manufacturing
Technological transfer to Plastinov achieved for PBT vitrimer formulation
Determination of best vitrimer formulation for classical PBT processes (1% vitrimer)
Determination of application for 2% vitrimer PBT: 3D printing

References :

[1] Demongeot A, Groote R, Goossens H, Hoeks T, Tournilhac F, Leibler L. Cross-Linking of Poly(butylene terephthalate) by Reactive Extrusion Using Zn(II) Epoxy-Vitrimer Chemistry. Macromolecules 2017;50:6117–27.

[2] Farge L, Hoppe S, Daujat V, Tournilhac F, Andr S. Solid Rheological Properties of PBT-Based Vitrimers. Macromolecules 2021;

2022

Research subject : Eco-design from MDF waste : advanced printable composites for furniture premium customization

Johan RAMAUX (1st year)

Cécile NOUVEL, Isabelle ZIEGLER-DEVIN, Arnaud BESSERER

Axe PRODUCT ENGINEERING | LERMAB | Acta Mobilier

Keywords : 3D printing, Wood composite, Medium Density Fiberboard, Recycling, Thermoplastic

General context, scientific issues :

Medium Density Fiberboard is one of the most widely used materials for furniture. Every year, nearly 40 million m³ are wasted worldwide. [1] Acta Mobilier produces large quantities of Medium Density Fiberboard (MDF) waste, mainly sawdust. Recycling this material is a double opportunity to offer its customers new products, and to improve environmental responsibility. The creation of a new product via an additive manufacturing process has an overwhelming advantage as it allows the fabrication of unique products.

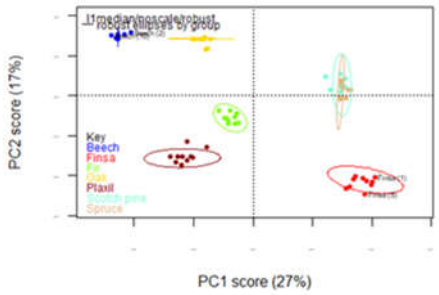
Objectives and stakes :

The general objective of this thesis is the production of a printable bio-composite including MDF sawdust. The main challenges will be to re-use as much sawdust as possible in the printable composite material and to ensure the printability of it. Procurement of MDF is changing every day, so sawdust is changing too. This is why, the variability of sawdust will be studied as well as its impact on the final product.
In order to offer a new product to the furniture industry, the material will have to comply with various European standards. Moreover, the ability to 3D print the composite will offer a wide range of customization to customers.

Methodology :

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

Illustration : Principal Component Analysis of different wood panels issued from different wood species. Purple and light green groups are the main types of MDF waste used.



Main results

MDF sawdust has been characterized with different methods. Using near infrared spectroscopy (NIRS) coupled with a PCA (cf. figure), a classification of different waste batches (issued from various origin and thus containing different wood species) was obtained. To perform the PCA, spectra need to be compared with data for a database [2]. Subsequent computation by PLS-R allowed the modelling of the sawdust mix content and the determination of the relative amount of raw material from each supplier in the first batch of MDF sawdust. In the same time, we have studied the feasibility to mix PLA and MDF. Indeed, various tests have been carried out in order to see what problems need to be solved. Preliminary results showed that the main issue was not compatibility between the polymer matrix and the MDF sawdust but rather the printability of the bio-composite. The amount of sawdust seems to be one the main limiting factor. In the future, the printability of the composite will be improved. Moreover, the increase in MDF amount in the bio composite is one of the main short-term objectives

References :

[1] Couret, Laetitia, 2017. Fractionnement de déchets de panneaux de bois MDF post-consommation par voie chimique pour la réalisation de matériaux biosourcés à haute valeur ajoutée. Thèse. Génie des Procédés. Ecole Centrale de Nantes.
[2] Schwanninger M, Rodrigues J-C, Fackler K, A Review of Band Assignments in near Infrared Spectra of Wood and Wood Components – Journal of Near Infrared Spectroscopy, 2011, Vol.19, Issue 5, 287-308

2022

Research subject : Effect of the emulsification process on the stability and rheological behaviour of Pickering emulsions : impact of the particles distribution between interfaces and volume

Ramos Diego Mauricio(4th year)

Roques-Carmes Thibault, Sadtler Véronique

Axe PRODUCT ENGINEERING

Keywords : Pickering emulsions, reverse, direct emulsions, emulsification process, partially hydrophobic silica, ultrasonic homogenizer, rotor-stator mixer, interfaces, material balance.

General context, scientific issues :

In 1903, Dr. W. Ramsden claimed that the presence of a colloidal solid at a liquid-liquid interface could produce a persistent emulsion. In 1907, the work of Dr. S. U. Pickering proved that the solid particles could stabilize an oil-in-water emulsion. Indeed, the adsorption energy of the particles at the interface is very high, which is an interesting characteristic since the solid particles can form a coating around the droplets of the disperse phase. The particles can be functionalized in order to respond to an environmental stimulus. Thus, an active ingredient could be encapsulated in the droplets of the disperse phase and then delivered in a specific organ of the body. A lot of works focus on the formulation of the Pickering emulsions but the influence of the process is not fully studied. The aim of this work is to study the production process of the Pickering emulsions and to establish its relation with the formulation parameters.

Objectives and stakes :

- Study reverse and direct emulsions prepared with the same silica particles.
- Quantify the particles distribution between the liquid interfaces and the bulk as a function of the emulsification energy and emulsion nature.
- Establish a mathematical model describing the emulsion rheological behaviour as a function of the emulsion droplet size and the rheology of its continuous phase.

Methodology :

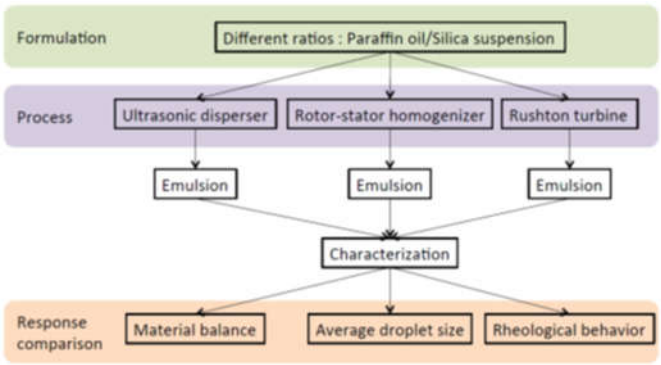
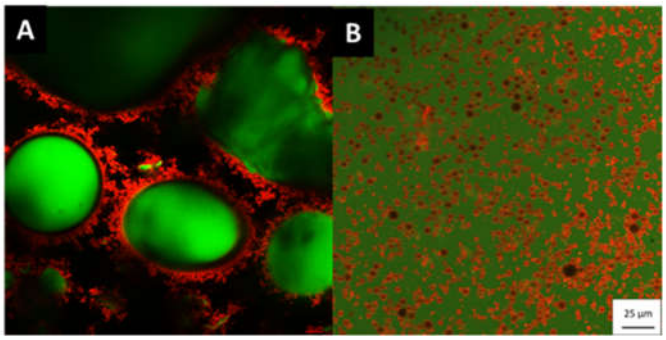


Illustration : Confocal pictures of (a) reverse and (b) direct emulsions



Main results

Water-in oil reverse and oil-in-water direct emulsions were prepared with a rotor-stator mixer and using the same partially hydrophobic silica particles. Both kinds of emulsion were stable.
Reverse emulsions showed the smallest average droplet diameter. The relative viscosities or elastic moduli of these emulsions exhibited the highest values.
In order to find the influence of the non-adsorbed silica in the rheological behaviour of Pickering emulsions, its fraction in the continuous phase is experimentally determined. Then a material balance may be calculated on the whole emulsion system. This material balance will help to elucidate the origin of the Pickering emulsions stability against coalescence: are the droplets fully covered by the silica aggregates? Does the process change the silica coating characteristics?

References :

[1] PICKERING, S.U., Emulsions, J. Chem. Soc. 91 (1907) 2001 -2021.
[2] L. Ridel, M.A. Bolzinger, N. Gilon-Delepine, P.Y. Dugas, Y. Chevalier, Pickering emulsions stabilized by charged nanoparticles, Soft Matter, 12 (2016) 7564-7576.
[3] W. J. Ganley, J. S. van Duijneveldt, Steady-state droplet size in montmorillonite stabilised emulsions, Soft Matter 12 (2016) 6481.

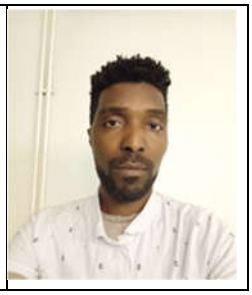
2022

Research subject : : Modelling of rheologically evolving fluids

Adilson SAMBA (1st year)

Cécile LEMAITRE, Philippe MARCHAL

Axe PRODUCT ENGINEERING



Keywords : Thixotropy, Viscoelasticity, Time-dependent fluids, Structural modeling, Numerical simulation, Viscosity, Shear rate, Shear stress, Yield Stress, Herschel-Bulkley model, Regularization

General context, scientific issues :

Many industrial products (cosmetics, paints, food, etc.) exhibit complex rheological behaviors such as shearthinning, viscoelasticitic or thixotropic behaviors. In order to manufacture correctly these products and to provide them the desired use properties, it is necessary to understand their rheological behavior. Thixotropy 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 & Wagner, 2009). A rheological behavior model is associated with this structural kinetics, such as the Houska model (Houska, 1981) for thixotropic yield stress fluids

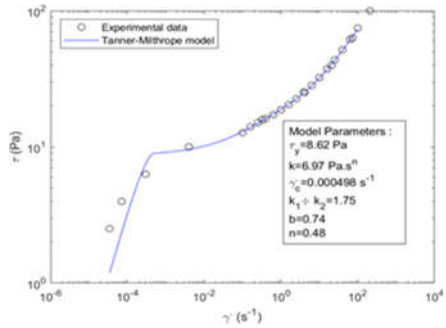
Objectives and stakes :

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

Methodology :

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

Illustration : Comparison of the proposed model with the experimental flow curve of Nivea body lotion.



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. Here-after the proposed model in a scalar form :

If $\dot{\gamma} \geq \dot{\gamma}_c$

$$\tau = \tau_y + k(1+\lambda^b)\dot{\gamma}^n$$

If $\dot{\gamma} < \dot{\gamma}_c$

$$\tau = \tau_y\left(2-\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)\frac{\dot{\gamma}}{\dot{\gamma}_c} + k(1+\lambda^b)\dot{\gamma}_c^{n-1}\left[(2-n)+(n-1)\frac{\dot{\gamma}}{\dot{\gamma}_c}\right]\dot{\gamma}$$

where λ is governed by Moore kinetics:

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

with τ the shear stress, $\dot{\gamma}$ the shear rate. The model parameters, the yield stress τ_y, the consistency k, the flow index n, the two kinetic constants k_1 and k_2, and parameter *b* are optimized to best fit the experimental data.

References :

Houska, M. (1981). Engineering Aspects of the Rheology of Thixotrpic Liquids.

Mewis, J., & Wagner, N. J. (2009). Thixotropy. Advance in Colloid and Interface Science, 214–227

2022

Research subject : Flowability and interparticle forces in granular materials

Andrea Suaza Montalvo (3rd year)

Véronique Falk, Maria Graciela Cares

Axe PRODUCT ENGINEERING

Keywords : Granular compaction, flowability, handling, characterisation

General context, scientific issues :

Granular materials are used in a vast number of industries and daily life. A persistent problem in the industry is related to the flow of cohesive powders, which is usually poor [1]. The flow behaviour, or flowability, is quite challenging to characterise. The complexity of the link between local particle interactions and their global macroscopic behaviour has undermined granular flows understanding, remaining, even nowadays, essentially empirical [2]. Understanding the role of interparticle forces is essential to apprehend powder flowability. With this thesis, we aim to look for new ways to describe granular flow through the macroscopic flow properties of the powder, and attempting to develop some hypothesis about the relationship between this macroscopic behaviour and interparticle interactions. The primary objective is to ensure process feasibility without compromising other important aspects such as safety, health, and economy.

Using a multidisciplinary approach, we propose a method to characterise granular flow, by an original approach based on the energy supplied to powders under vibration.

Objectives and stakes :

- Propose the role of particle interactions in powder flowability from the bulk analysis.
- Quantify and relate bulk forces to flowability through an energetic analysis.
- Relate particle properties to bulk behaviour and associated phenomena.

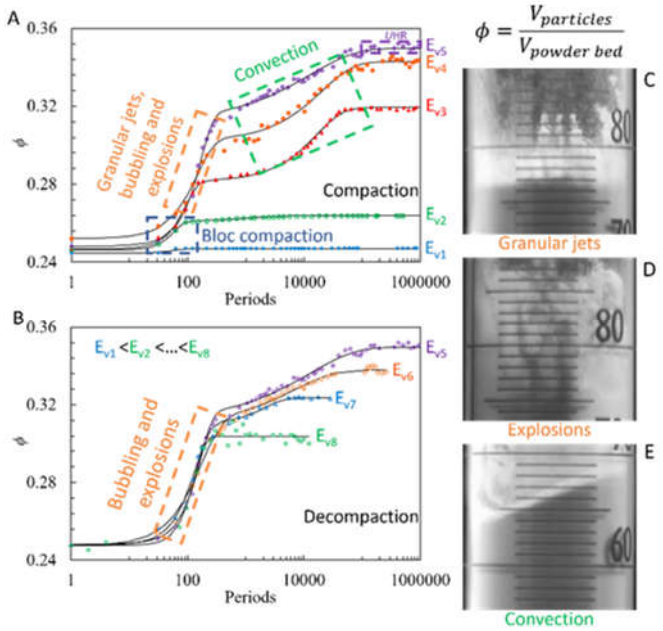
Methodology :

We have focused our efforts on analysing powder compaction by vibration as a method to evaluate powders' flowability [3]. Using a particle damper, we control the amount of energy supplied (Ev) to the powder bed, observing the different phenomena, and the bed high evolution as a function of time.

The description of granular flow through energy values allows to extrapolate the flow behaviour and predict which phenomena could be observed in different configurations, targeting process description.

From this energetic approach, based on the bulk behaviour analysis, we will propose some relations between particles characteristics and powders flow behaviour.

Illustration : Granular compaction of Avicel® PH102



Main results

Previous works show that the amount of energy supplied to a powder bed significantly influences its compaction and flow behaviour [3-4]. As the energy provided to the granular media increases, the bulk compacts until reaching a maximal steady-state packing density (UHR, Fig. 1A). After this point, bigger energies will result in less compacted or fluidised granular beds (Fig. 1B). The many phenomena observed during compaction are a function of the quantity of energy provided to the granular material. In general, when low energies are supplied, the granular media will compact calmly, and the contact force networks seem not to change. When the energy supplied increases, granular jets (Fig. 1C), bubbling, and even explosions (Fig. 1D) can appear during the first periods of compaction, while a convection phenomenon (Fig. 1E) can be observed during the second step of compaction. If even more energy is supplied, the reorganisation will be affected, and at some point, under UHR, the powder bed will fluidise. Here, interparticle forces seem to be inferior to the energy provided to the media, giving rise to a fluidised bed where volume changes are observed

References :

[1] J.M. Valverde Millán. Pow. Flow (2013). [2] T. Kojima, J.A. Elliott, Chem. Eng. Sci. 101 (2013). [3] A. Saker et al. Powder Technol. 354 (2019) [4] M.-G. Cares et al. Int. J. Pharm. (2021).

2022

Research subject : Open-source additive manufacturing for multi-material plastic recycling in short circuit

Catalina Suescun Gonzalez (1er year)

Hakim Boudaoud, Cécile Nouvel, Joshua Pearce

ERPI UL / LRGP UL Axe PRODUCT ENGINEERING | Electrical & Computer Engineering department Western University, Canada

Keywords : Additive fabrication, open source, circular economy, recycle, plastic multi-material.

General context, scientific issues :

Based on projections by 2050 plastics in the oceans will overweight fish and the global plastic production is expected to increase to 850 million tons per year by the same year [1]. Past researches demonstrated that using distributed recycling fits into the circular economy paradigm [2]; i.e. consumers directly recycle their own waste, so recycling is done at a local scale, reducing waste associated to transportation and retail.

Additionally, resent initiatives have propose a new approach based on these distributes plastic recycling for open-source 3D printing to help the plastic waste utilization called DRAM Distributed recycling and additive manufacturing [3]. However, every time that the material is melt and then solidified the mechanical properties of the resultant 3-D print decrease. Other limitations include, impurities found in waste as well as contamination or mixture with incompatible polymers, which complexify the recycling process. Indeed, the impurities reduce the rheological properties while incompatibilities increase the material heterogeneity and thus. Both lower the mechanical properties affecting the quality of the resulting object and worsen the plastic waste process.

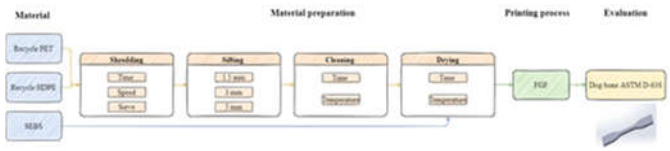
Objectives and stakes :

The thesis aim is to solve the current issues presented in the local scale plastic recycling by direct printing technology;
1. Evaluation the direct printing of recycled multi-material polymers via Fused Granular Fabrication (FGF).
2. Fabrication of an open-source melt flow index for rheological properties evaluation before printing.
3. Compatibilization and characterization of Polyethylene terephthalate (PET) and incompatible polymer contaminant.
4. Evaluation of the use of compatibilizers for printing purposes.
5. Proposal of a sustainable and economical process for mixed plastic printing.
6. Fabrication of large-scale objects via FGF with recycled multi-materials mixtures.

Methodology :

1.Obtention of the recycled raw material with easy implementable operations at local level: -Collection, shredding, sifting, cleaning and drying.
2.First experimental assays of printability and optimization of the printing parameters.
3. Elaboration and characterization of polymers blends using compatibilizer.
4. Evaluation and validation of the blends in 3D printing.
5.Optimization of the properties of the final printing objects.

Illustration : Global framework of the experimentation



Main results

At first, a systematic biographic analysis has been carried out regarding the compatibilization between PET and incompatibles polymers to determine the most appropriate compatibilizer for our study. From the analysis concerning PET an polypropylene, reactive compatibilizers using Maleic anhydride functionalized polymers were the most commonly used followed by non-reactive copolymers such as Poly (Styrene-co-Ethylene-co-Butylene-co-Styrene) copolymer (known as SEBS). After redirect my study towards a large significant problematic, the separation and storage of plastic waste, the blend between PET and High density polyethylene (HDPE) needs further bibliographic analysis. However, compatibilizers appear to be similar of those found for PET and PP blends.
To begging with the experimental tests, raw material was obtained following the framework of the experimentation. Both, PET and HDPE were shredded, sifted, cleaned and dried to be later printed. First results on the obtained raw material after all those steps showed that the direct printing of recycle multi-material without compatibilizer seems feasible if the accurate granulometry is obtained after treatments. Three different sifters sizes were used to determine the best appropriate granulometry of the particles. Optimization of the parameters have also been experienced. However, from the results obtained until now the repeatability, accuracy and properties of the final 3D printed pieces require further investigation

References :

[1] Godswill, A. C. & Gospel, A. C. Impacts of Plastic Pollution on the Sustainability of Seafood Value Chain and Human Health. 5, 93 (2019).
[2].Zhong, S. & Pearce, J. M. 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).
[3] Pavlo, S., Fabio, C., Hakim, B. & Mauricio, C. 3D-Printing Based Distributed Plastic Recycling: A Conceptual Model for Closed-Loop Supply Chain Design in 2018

2022

Research subject : Modeling of chemical and biochemical processes using advanced phenomenological and data-driven techniques

Cindy Trinh (2nd year)

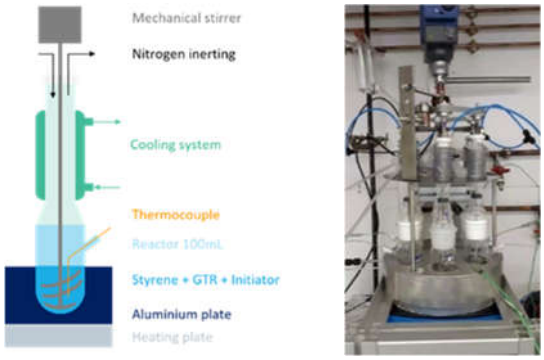
Axe PRODUCT ENGINEERING

Keywords : artificial intelligence, machine learning, chemical product design and engineering

General context, scientific issues :

Chemical Product Engineering (CPE) has numerous challenges such as the complexity of the products and of the link properties-structure-ingredients-process, as well as the necessity to discover and develop quickly new products and properties. In recent years, artificial intelligence (AI) and machine learning (ML) data-driven methods have gained increasing attention due to data explosion and technological breakthroughs. These methods have shown very good performance in tackling particularly complex problems in other areas (computer vision, natural language processing…) and could therefore be very helpful to address CPE challenges, where classical approaches fail or are inefficient

Illustration : Experimental set-up for radical polymerization of styrene in presence of GTR powder (Application 1)



Objectives and stakes :

This research focuses on the application of ML approaches in CPE. In particular, the objectives are to understand the characteristics of ML methods, provide guidelines in applying them given problem and data specificities and identify their limits and challenges. Two applications, where using ML methodology could greatly help, are under study:

• The first application consists in the modeling of radical polymerization of styrene in presence of Ground Tire Rubber (GTR) powder [1]. Why ML? Phenomenological (i.e., knowledge-based) modeling is particularly complex for this system (a lot of reactions and nonlinear phenomena occur simultaneously) and the grafting of polystyrene on GTR is not completely understood.

• The second application is done in collaboration with the department CITHERE [2]. The goal is to predict the thermochemical properties (enthalpy and entropy of formation) of a molecule from its molecular descriptors. Why ML? Quantum Chemistry or Group Contribution methods, commonly employed to calculate these properties, have shown limitations in terms of applicability to more complex or larger chemicals and/or computational costs. Comparing the results from different methods also guarantees more reliable property predictions

Methodology :

• Application 1: First, an experimental procedure enabling a homogenous and controlled polymerization must be set up to produce enough data of good quality, necessary in any ML approach. Based on the obtained data, several ML techniques can be evaluated and combined with phenomenological models.

• Application 2: Data from public databases (ex: DIPPR) are used to construct the ML prediction model. First, relevant molecular descriptors (i.e features influencing thermochemical properties) must be identified, extracted from molecules and preprocessed. Several ML techniques can then be evaluated

Main results

• The state-of-the-art of ML in CPE resulted in a review article [3].

• Application 1: To produce enough data, a system was designed to perform 6 polymerizations in parallel (Illustration 1). To ensure data quality, several points were addressed such as agitation, temperature, reactor design and design of experiments while special attention was paid to the calculation of uncertainties and losses during the experiments. The obtained data consist in different input operating conditions (temperature, time, reactants composition) and the respective output product characteristics (styrene conversion, grafting efficiency and polystyrene molecular weight). Several pure ML models are being investigated as well as hybrid ML/phenomenological models to combine their precision and explicability respectively.

• Application 2: The software AlvaDesc was selected to calculate 5666 molecular descriptors of DIPPR's 2230 molecules. The library RDKit was used to convert molecules from SMILES to MDL MOL format, the latter containing 3D information necessary for some descriptors. Then, a holistic approach was implemented to evaluate the impact of diverse preprocessing methods and scenarios as well as ML models on the prediction performance. In particular, specific methods were used to deal with this high dimensionality and scarce dataset and descriptors' physical meaning was investigated deeper to justify if their choice is relevant. Different methods were also tested to identify the most impactful descriptors. An article and an oral communication at ESCAPE 32nd congress are in preparation

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2022

Research subject : Salts and pollutants management in supercritical water gasification processes

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Keywords : Supercritical water, gasification, inorganic salts, pollutants, energy, hydrogen, biofuels, black liquor, process engineering.

General context, scientific issues :

A promising energy recovery process for very wet or even liquid resources is gasification in supercritical water to produce energy valuable gases (a mixture of H2, CH4 and CO2). Supercritical water gasification is based on the properties of water under high pressure and temperature. Beyond its critical point (over 374°C and 22.1 MPa), water becomes a highly reactive medium and promotes gasification reactions. In this process, contrary to dry gasification, it is not necessary to dry the resource beforehand. This allows to maintain water as reactant and it also avoids energy losses due to the drying step. Among the resources targeted by this process, we can cite for example waste from the food industry (fruit pomace and brewers' spent grains, vinasse...), industrial effluents (black liquor), microalgae, methanation digestates, sewage sludge... This thesis focuses on black liquor which is largely available and which is a good candidate to study issues linked to inorganic content of wet resources

Objectives and stakes :

The development of the supercritical water gasification process is at the laboratory pilot stage, the largest continuous reactors developed being of the order of 100 L/hour, with operating times limited to few hours. Research and development actions are still necessary to further its development to an industrial scale. The main issues and lines of research are: energy supply and recovery, conversion efficiency of carbon into valuable gases (H2 and/or CH4), corrosion problems, resistance of the materials, pumping and high-pressure injection of solutions containing suspended solid particles and finally management of pollutants (such as H2S) and inorganic species (salts). This thesis deals with this last point. The evolution of the dielectric constant and the ionic product of water when reaching the supercritical state leads to the precipitation of salts contained in the resource [1]. This phenomenon of precipitation of salts in solid or liquid form often leads to the clogging of the reactor [1-2]. This study will focus on solutions to understand the behaviour of these salts and their management, while taking into account the constraints. Another major problem concerns pollutants. Originating mainly from organic matter, gases such as H2S are very toxic and corrosive, inducing problems downstream in the process. One solution would be to capture these gases in inorganic salts during gasification or prevent them from forming thanks to the use of additives. It is also possible to add a gas cleaning step at the reactor outlet. These phenomena have been very little studied and characterized in the literature and yet they constitute one of the major challenges for the development of these processes, particularly for resources rich in salts and sulfur such as black liquor

Main results

Some salts precipitate directly under supercritical conditions (type-2 salts) while others can still be dissolved near critical point (type-1 salts). Literature shows that one way to remove salts out of reactors is to make the inorganic mix tend to a type-1 salt behaviour, playing on elements ratios [3-4]. In this case, most of the salts can be solubilized by water and then removed as a salt-rich effluent after cooling at the bottom of devices, instead of being stuck on reactors' walls. The work is composed of both simulations and an experimental approach. Model mixtures of salts, according to the resource composition, are first studied with the use of additives in batch reactors to build a numerical model of global behaviour (work in progress) before looking for management solutions on real resources and continuous devices.

Illustration : Precipitation of sodium carbonate in a continuous hydrothermal gasification reactor, LITEN.

Methodology :

First, a bibliographical study was carried out concerning the salts, their behaviour in supercritical water gasification, the formation of pollutants and the solutions implemented in the literature. A second part of the study concerned the thermodynamic approach: the laboratory has thermodynamic equilibrium calculation tools (Factstage, Gemini...) which allow predicting the behaviour of inorganics (equilibrium diagrams of solid, liquid or gaseous phases as a function of temperature and pressure conditions). It is necessary to evaluate whether these tools and the thermodynamic databases are valid under conditions of supercritical water gasification. These tools can lead to a better understanding of the behaviour of the inorganic species. In parallel, the experimental work focuses on the characterization of resources and gasification products by all the necessary analytical means, with a special focus on inorganics. Black liquor is the resource studied in this project. This resource is available in the laboratory within the framework of the European Pulp&Fuel project, currently in progress. A second experimental part of the thesis concerns the definition of a device to characterize the behaviour of salts in supercritical conditions. The laboratory currently has two devices dedicated to supercritical water gasification: a batch reactor (volume 500 mL) and a continuous reactor (capacity 10 L/h). The idea was first to propose an adaptation of one of these two devices. The ultimate goal is to increase the understanding of the behaviour of salts and pollutants in supercritical water conditions. With this knowledge, an evaluation of the different strategies for inorganics and pollutants management is expected, whether thermodynamically or chemically, and thus help the laboratory to propose design solutions for future supercritical water gasification pilots.

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2022

Research subject : Designing emulsions stabilized with proteins: probing interfacial properties of Pea protein-stabilized emulsions

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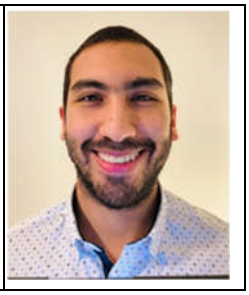


Keywords : Emulsions, Rheology, Pickering Emulsions, Soft Matter, Proteins, Interfaces

General context, scientific issues :

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

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

Objectives and stakes :

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

Methodology :

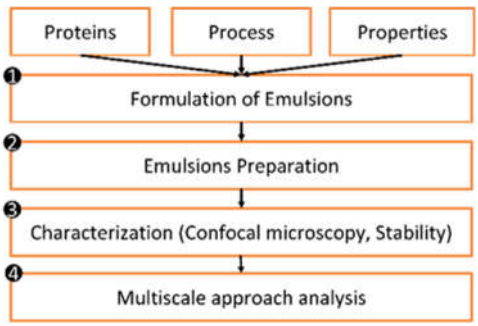
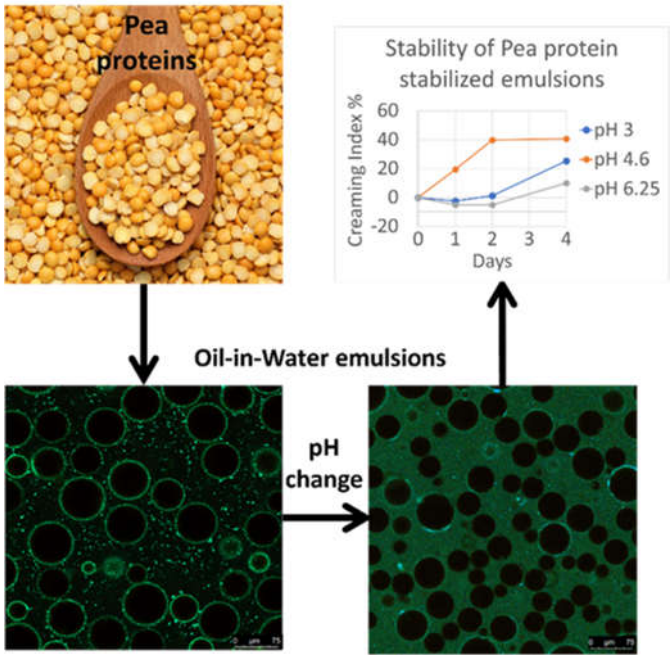


Illustration : Schematic representation of the protocol followed with protein-stabilized Pickering emulsions



Main results

Based on previous results obtained with animal-based proteins of Bovine Serum Albumin, a simple protocol to stabilize Silicone oil-in-water emulsions was implemented.
The emulsions were visualized with confocal microscopy by means of molecular rotors attached to the proteins. The stability of the emulsions was studied for several days. A characterization of the elasticity of the interfaces was performed by means of the molecular rotors, as well as an observation of how the stabilization mechanism varies as a function of a key property such as pH.
The results show a correlation between the elastic character of the interfaces and the stability of the emulsions, thus relating the mesoscopic scale to the macroscopic properties.

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