

Presentation of PhD and Post-doctoral research works

2017



Presentation of PhD and post-doctoral works at LRGP

This document presents the thesis and the postdoctoral research works realized at LRGP.

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:

- Processes for Environment, Safety and Resource Valorization
- Intensification, Optimization and Architecture of Processes
- BioProcesses - BioMolecules
- Kinetics and Thermodynamics for Energy
- Processes for Products and Materials

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. It is also a wish to ensure that every researcher can communicate on equal ground.

I wish you a pleasant reading!

Laurent FALK

Director of Reactions and Chemical Engineering Laboratory, Nancy, France

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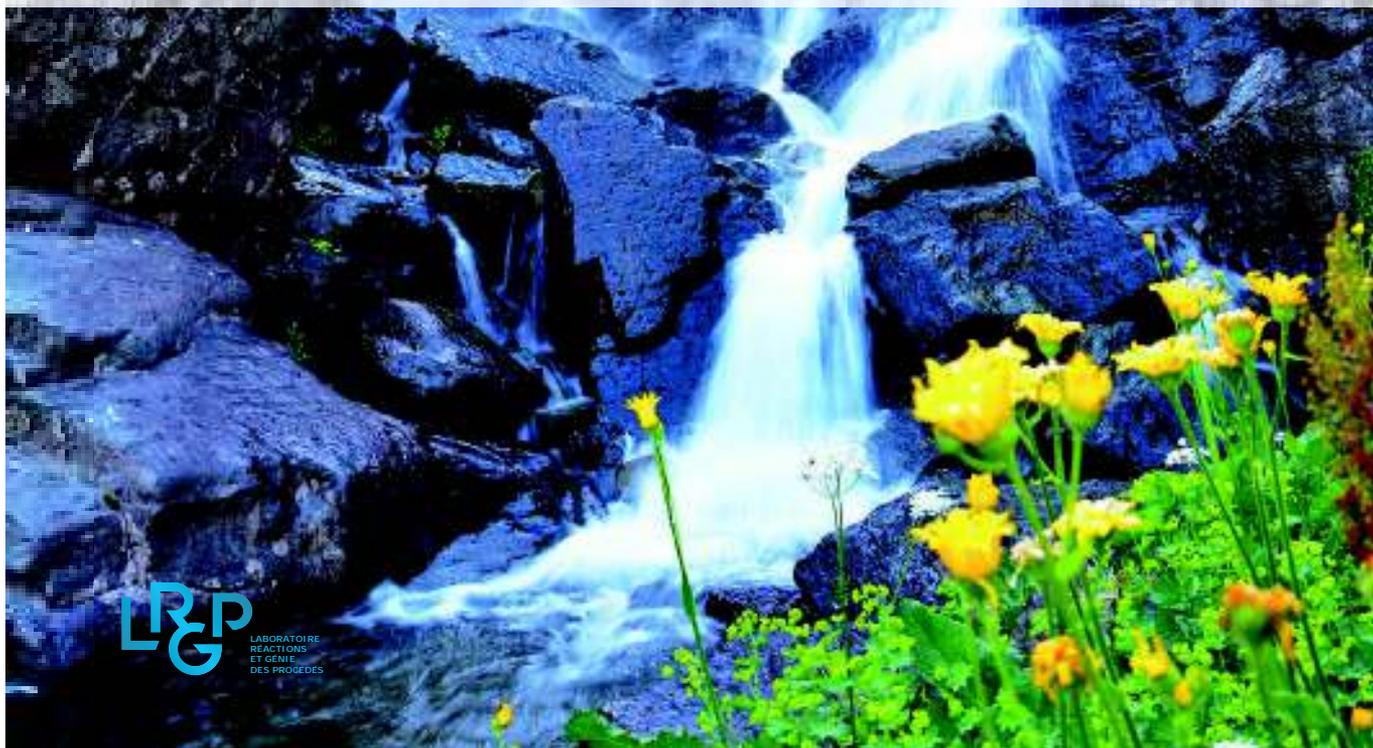
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PERSEVAL

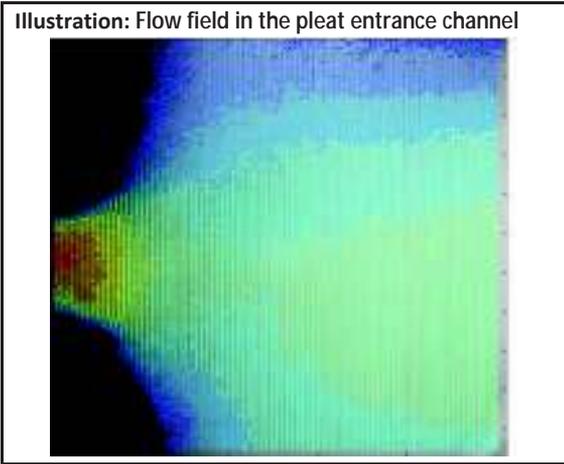
PROCESSES FOR ENVIRONNEMENT,
SAFETY AND RESSOURCE VALORIZATION



2017 	<u>Impact of airflows induced by the filter media pleating on clogging phenomena for steady and transient states</u> ALILOU Youssef (3 nd year) Supervisor: THOMAS Dominique, BARDIN-MONNIER Nathalie AXE 1 SAFE	
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Keywords: HEPA filter, pressure drop, modeling, simulation

General context, scientific issues
 Containment of airborne contamination in hazardous industrial activities is mostly ensured by HEPA filters. It's essential to be able to predict the evolution of pressure drop of these filters to anticipate any dysfunction or failure of these devices. The pressure drop is linked to airflow rate and to clogging process. For pleated filters, pressure drop increases quickly due the loss of filtration surface, this phenomenon is called surface reduction [1]; its study is the purpose of this thesis.



Objectives and stakes
 The purpose of this thesis is to enhance the comprehension of pleated filters' behavior and to characterize the surface reduction phenomenon caused by particle deposit inside the pleat. Finally we aim to develop predicting models of clogging in both transient and permanent regimes.

Main results
 Based on the flow modeling, a pressure drop model for the clean filter has been developed and validated using experimental data for different kind of filters (HEPA, ME) with different geometries. Experimental measurements of the HEPA filter pressure drop during clogging have been realized and are used to validate numerical models. A pressure drop model that characterizes the surface reduction of the filter during heavy clogging is under development.

Methodology / Experimental approach
 A methodology divided into two parts has been fixed for the running of this project. Firstly, we aim to characterize the flow within the pleats of HEPA filters. Using optical diagnostics we measured the flow field within the pleats. The experimental data have been used to validate numerical flow calculation (ANSYS CFX, GeoDict). Using these numerical tools, a data bank has been established and used to model the flow in the filters and to estimate the resulting pressure drop at the pleat scale. Secondly, we will measure the evolution of pressure drop of the filter during clogging; an experimental bench has been developed in that purpose. Numerical models will be enhanced and validated upon grid tests.

References
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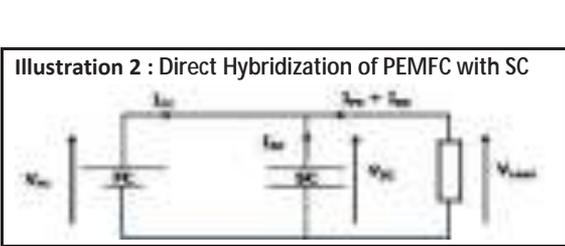
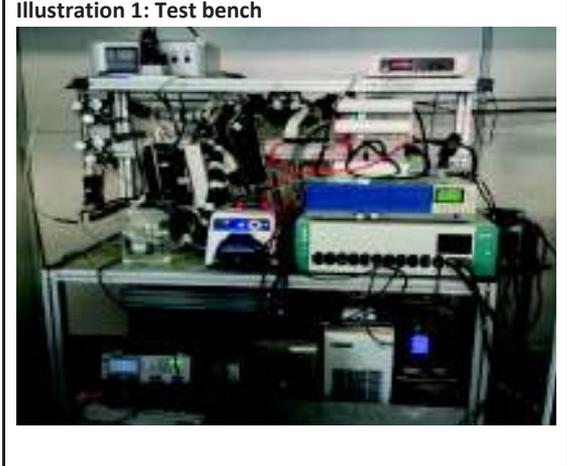
2017 	PhD subject : Direct hybridization of a PEM fuel cell to a supercapacitive storage elements - comparative study of the ageing in urban cycling mode and optimal management of hydrogen consumption <u>Divyesh ARORA</u> <u>Prof. Stéphane RAEL Dr. Caroline BONNET</u> Axe 1 SYSPOL	
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Keywords : PEMFC, Supercapacitors, Direct hybridization, FC-DLC, hydrogen economy

General context, scientific issues
 It can be observed a pragmatic shift in the automobile industry for the acceptability of electric motors over internal combustion engines because of the higher efficiency, reduced tail pipe emissions, growing concern for depleting fossil fuels and also energy security. In this category fuel cell cars being most efficient in general and PEMFC cars may appear most appealing in particular. Nevertheless, PEMFC has some drawbacks [1]. However, direct hybridization of PEMFC with supercapacitors (SCs) solves them efficiently [2].

Objectives and stakes
 The direct hybridization of a fuel cell to a supercapacitor allows better management of the transients induced by sudden change in the electricity demand, while avoiding the presence of power electronics converters.
 The PhD subject proposed is focused on (i) the investigation of the degradation of the fuel cell core (diffusion layers, electrodes, membrane) depending on its hybridization state and (ii) research of the optimal strategy for hydrogen supply to the cell for a given performance.

Methodology / Experimental approach
 Long term tests will be carried out on an existing test bench, with evaluation of degradation extent and causes. Besides, modelling with its experimental validation, of the laws for control of the hydrogen flow rate is developed for the sake of the minimal hydrogen consumption.



Main results
 H₂ can be reduced through various suggestions such as by changing the reference of control of gases from load cycle current to the fuel cell current measured during the cycle as SC can provide the mitigation and avoid the condition of starvation of gases. Secondly, it can be reduced by utilizing the energy wasted during cycle for charging the SC during transient phase. It can be done by introducing another parameter such as minimum current corresponding to the H₂ flow rate. If I_{FC} is less than minimum current corresponding to the H₂ flow rate, flow rates are set to minimum current corresponding to the H₂ flow rate. Thus, excess of H₂ is being utilised for charging SC and finally, by increasing the storage capacity, which can be realised by increasing the number of SCs [3]. From no SC to 3 SCs, the gain in H₂ consumption is nearly 16 %. Increasing the number of SCs from 1 to 3 allows a gain in H₂ consumption by nearly 5%.
 Next concern is to investigate the degradation of the fuel cell core with respect to state of hybridization. By and large, it has been examined that increasing the number of SCs does not affect the degradation of fuel cell. However, other parameters need to be scrutinized in the future.

References

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2017



Relationship between the variability of urban pollution and geographic and socio-cultural traits in Benin and France

Nelly Chrystelle Houéfa ATINKPAHOUN (3rd year)

Marie-Noëlle PONS, Henri H. SOCLO

Axe 1 | Sols & Eaux |



Keywords: Wastewater treatment ; Variability urban wastewater pollution.

General context, scientific issues

Depending of their origin, wastewater are characterized by a high variability of flow and composition. Improving the performance of treatment plants requires large-scale measurement campaigns which are expensive. To cope with these difficulties, it is important to develop models for predicting the flow and composition of these wastewater. This requires, first of all, having information on the daily variation of the wastewater flowrate and pollution load. It is in this perspective that this study has been conducted on two experimental sites and for a wide range of pollutants.

Objectives and stakes

The objectives are to study daily variability of wastewater entering the Maxeville wastewater treatment plant in "Grand-Nancy" in France and of wastewater entering "Vie-Nouvelle" city at Cotonou in Benin. In medium or long term, the experimental data from this study will allow the development of a methodology as simple as possible for the prediction of the variability of wastewater.

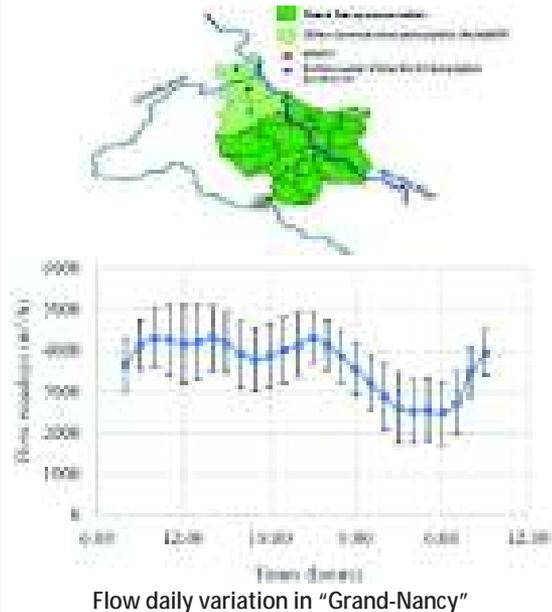
Methodology / Experimental approach

- Literature review: state of the art on the subject, pollution parameters and geographical, socio-economic and cultural catchment ("Grand-Nancy" and Cotonou) characteristics ;
- Sampling campaigns; Statistical data processing ;
- pH modelling ;
- Simulation of wastewater composition on the study sites.

COTONOU



GRAND-NANCY



Main results

During the day, "Grand-Nancy" loses 12% of its active population who go to work outside the catchment. However, 81% of active population come from outside the catchment for daily work. Thus, a large population is present in the agglomeration throughout the day. This is reflected very well through the variations in wastewater flow and organic pollution, which present three peaks on the day reflecting the day's activities (morning, noon and evening) from these populations. Also the flow and pollution load, is reduced during the weekend compared to the weekdays due to the decrease of the population.

The wastewater of « Vie-Nouvelle » at Cotonou is characterized by a great variability of pollution, especially during daytime. Organic pollution during the night-time period presents high concentrations or concentrations of the same order as that of the daytime, which is not in accordance with the typical profile of wastewater. Overall, these wastewaters are not in compliance with discharge standards, especially with regard to macropollution. Then, they require treatment before discharge in the environment.

References

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<p>2017</p> 	<p>Hybrid Geomaterials and Photocatalysis: An Efficient Procedure for Depollution of Water</p> <p>Hawraa Ayoub (3rd year PhD)</p> <p>Thibault Roques-Carmes, Olivier Potier Axe 1. SOLEO</p>	
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Key words : Micropollutants quantification, LC-MS/MS, Iron impregnated Faujasite Y

General context, Scientific issues

Micropollutants are defined as chemical or material existing at very low concentration that have a recognized potential or real threat to human health or the environment. Over the last few decades, the presence of micropollutants in the aquatic environment gained an increasing environmental concern for becoming a worldwide issue. Micropollutants consist of a variety of different substances including pharmaceuticals, personal care products, industrial chemicals, pesticides, etc [1]. These compounds are present into the different aquatic systems, such as surface water of rivers, groundwater and even drinking water, at concentrations between few ng/L and several µg/L [2].

Objectives and stakes

First, our goal was to develop an efficient analytical procedure needed to identify the micropollutants generally present in river water and quantify their range of concentration.

Second, the investigation of an efficient catalyst to be used in photocatalytic reactions, for the removal of a real cocktail of micropollutants of river water at very low concentrations. Photocatalytic reactions on model compounds: Phenol and Diclofenac were tested using the developed catalyst.

Methodology/ Experimental approach

1. Sampling

Water samples from 5 different sites at different positions on Meurthe and Moselle rivers were analyzed, in addition to a drinking water sample.

2. Micropollutant Analysis

Detection and quantification of different micropollutants in the 2 rivers were studied by LC-MS/MS after filtration and preconcentration by SPE.

3. Catalyst Preparation

Development of the zeolite based catalyst was achieved.

4. Photocatalytic- Fenton Removal

Photocatalytic-fenton reactions using the developed catalyst were applied on the model compounds.

Illustration: Synthesis of Iron Impregnated Faujasite



Main results

- By using LC-MS/MS technique, the analysis of Micropollutants in Meurthe and Moselle rivers was carried:
 - Detected and Quantified micropollutants: Bisphenol A, Carbamazepine, Clarithromycin, Diclofenac, Erythromycin, Estrone, Ibuprofen, Ketoprofen, Lidocaine, Naproxen, PFOA, PFOS, Sulfamethoxazole and Triclosan
 - Below the limit of quantification: Carbamazepine-10,11-epoxide, Cyclophosphamide, Estradiol-beta, Ethynylestradiol, Sulfadimethoxine, Sulfadimidine and Sulfathiazole
- Faujasite-Y zeolite impregnated with iron (III) was employed as a catalyst to remove the micropollutants by photocatalytic-fenton process.
 - An optimization of the process parameters was conducted: Hydrogen peroxide concentration, the light wavelength (UV and visible) and intensity, the iron loading immobilized as well as the pH of the solution were investigated
 - Complete photo-fenton degradation of phenol and diclofenac was achieved using Faujasite containing 20 wt.% of iron, under UV light, and in solution containing 0.007 mol/L of H₂O₂ at pH 5.5.

References

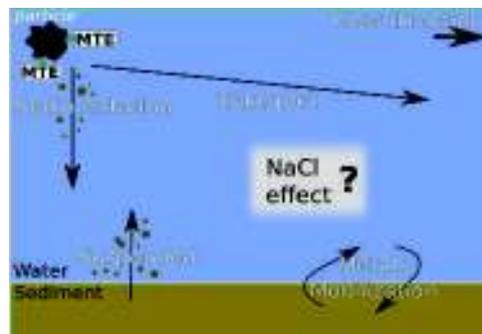
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<p>2017</p> 	<p>Metal trace elements and sodium chloride transfer dynamics in water-sediment interface in road retention basin</p> <p><u>Lucie Barbier (2nd year of PhD)</u></p> <p>Marie-Odile Simonnot, Ivana Durickovic (Cerema) Axe 1 SOLEO Cerema</p>	
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Keywords: Retention pond, NaCl, metal trace elements, transfer dynamics

General context, scientific issues
 During winter, deicing agents (mainly sodium chloride-NaCl-) are carried by runoff waters. They are collected by retention pond before being rejected into the environment. Yet, a high concentration of NaCl may have negative impacts on biodiversity. It may also affect water quality because of ionic strength that plays a major role on particles stability and on metals release [1]. Metals associated to particles may be released into pond water [2]. Therefore, the retention pond only delays the release of sodium chloride and dissolved metals into the environment, affecting ecosystem quality.

Illustration: Schematic representation of major phenomena influencing particle stability and release of metal trace elements (MTE)



Objectives and stakes
 The objective of this work is to bring better understanding of the role of NaCl on the dynamics of pollutant transfer in a natural and uncontrolled environment. Retention of deicer salts and their impacts on basin are influenced not only by physicochemical interactions but also by hydrodynamics. Physicochemical data have been measured for several years [3] on a road retention pond (Chenevières, Grand Est). In order to assess the influence of the pond design, a second one will also be studied. This work includes data acquisition on the ponds, water and sediment characterization, investigation of sediment settling, hydrodynamics characterization and role of physio-chemical interactions on pollutant dynamics.

- Main results**
- In the course of the 1st year, the second retention pond was chosen, with a design different from the previous one.
 - The water and sediment characterization had allowed to highlight functioning different between both basins -including sediment distribution and water flow are different and water composition.
 - During this winter 2016-2017 some results have been obtained on deicer concentration and on deicer and MTE fluxes
 - As in the 1st basin, the relation between chloride concentration and conductivity was established on this new basin.
 - The deicer salt collected by basin depend on road design and meteorological conditions.

Methodology / Experimental approach
 The study focus on monitoring two retention ponds during 2 years. Water and sediment composition will be characterized and we look at concentrations of deicer agents, trace elements and major elements (such as anions, organic matters, cations). This measurements is done during different rain/snow events to comprehend relation between events and NaCl influence. In order to understand NaCl impact on settling and its link with trace metals and deicers, the settling velocities will be monitored at different NaCl concentrations. All these data will enable us to evaluate the variation of pond parameters depending on weather and their influence on hydrodynamics. That why, hydrodynamics will be represented by compartmental modeling.

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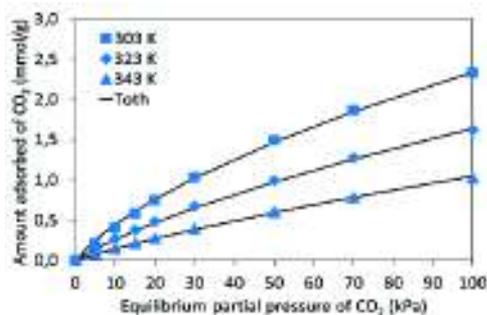
2017 	CO ₂ capture by an advanced process for its recycling <u>Sabrina BEDEL (3rd year)</u> Cécile VALLIÈRES Axe 1 SAFE	
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Keywords: energy, carbon dioxide capture, adsorption, recycling

General context, scientific issues

In recent years, anthropogenic carbon dioxide emissions have become an environmental subject of great concern because of the relevant influence of this greenhouse gas to the global climate change. As a matter of fact, there is an important need to control carbon dioxide level in the atmosphere. To this end, adsorption by porous materials such as zeolites, carbons or metal-organic frameworks is a promising and alternative way to reduce CO₂ emissions from large industrial sources, since this method requires lower energy consumption than the amine scrubbing.

Illustration: Comparison of the Toth predictions and the experimental data of CO₂ adsorption equilibrium



Objectives and stakes

The main purpose of this thesis is the development of an advanced adsorption process for capturing CO₂ from flue gases to recycle it. The different research areas are:

- Selection and characterization of one or more appropriate commercial adsorbent(s)
- Study and quantification of adsorption parameters in terms of equilibrium and kinetics
- Evaluation of the impact of impurities contained in flue gases on the adsorbent performances

Main results: Evaluation of equilibrium parameters

- Application of the temperature dependence form of the Toth model: prediction of adsorption equilibrium at any temperature by extrapolation or interpolation
- ① Six unknown parameters which have to be identified from the experimental data: q_{m0} , χ , b_0 , Q/RT_0 , t_0 , α
- Parameters estimability analysis: implementation of a sequential orthogonalization method [1,2] to assess which model parameters are the most estimable and in which order

$$q_{m0} > Q/RT_0 > t_0 > b_0 > \alpha > \chi$$

HOWEVER, the experimental information is insufficient to assess the parameter χ because a variation of 10% of its value implies a variation lower than 2% of the output

- ② The parameter χ is nonestimable and can be fixed
- Parameters identification study: computation of the optimal model parameters by using the experimental adsorption equilibrium data at 303 K, 323 K and 343 K
- ③ CO₂ adsorption equilibrium is satisfactorily predicted

Methodology / Experimental approach

- Evaluation of the textural (specific surface area, pore volume, pore size distribution) and physical (density, morphology) properties of the adsorbents to explain CO₂ adsorption phenomenon
- Adsorption equilibrium measurements to assess the amount of gas adsorbed per unit mass of adsorbent: static experiments carried out in a thermogravimetric analyzer (SETSYS Evolution apparatus)
- Adsorption kinetics measurements to determine the mass transfer rates from the gas phase to solid phase (breakthrough curves) : dynamic experiments carried out in a fixed bed adsorption unit
- Assessment of the material regeneration conditions in order to optimize the regeneration phase
- Quantification of the impact of impurities contained in flue gases in order to develop a specific and reliable adsorption model

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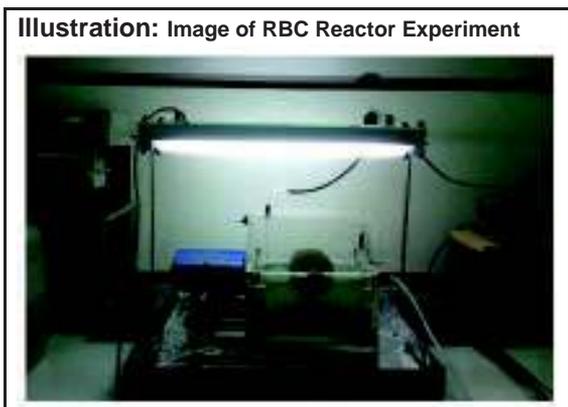
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<p>2017</p> 	<p>Coupling of bacteria and microalgae for the wastewater treatment and production of valuable biogas sludge</p> <p>BEJI Olfa (Second year of PhD)</p> <p>Supervisors name: Souhila PONCIN & Nouceiba ADOUANI & Huai Zhi LI</p> <p>Axe 1 SYSPOL</p>	
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Keywords: Multitrophic rotating biofilm contactor, sustainable wastewater treatment, opacity biofilm, microalgae-bacterial flocs

General context, scientific issues

Multitrophic rotating biofilm contactor (MRBC) technology represents a sustainable strategy using microalgae-bacterial flocs (MaB-flocs) within biofilm, where mineralization and photosynthesis are coupled in order to avoid O₂ supply and CO₂ production. In addition, sustainable remediation processes allow a low cost removal of wastewater nutrients and accumulate valuable biomass (for composting or anaerobic digestion) which improves the economic performance of this technology.



Objectives and stakes

In the present work, a lab-scale MRBC was designed to investigate multitrophic interactions between MaB-flocs and nutrients exchange. This should facilitate the biofilm-developmental process that controls the microbial population dynamics and shapes structured and well-adapted microbial ecosystems.

Main results

The evolution of opacity levels shown an increase between days 29 and 57 corresponding to mature biofilm attachment. The developed biofilm spontaneously partially detached from the discs after 57 days. Meanwhile the biomass production of flocs decreased. This can be explained by the lower density and the looser structure of the biofilm. In addition, the significant ammonium, phosphorous and COD removal rates of 82%, 76% and 83%, respectively have confirmed the biofilm accumulation and justify the communities' abundance of algae and bacteria in the reactor at a short HRT of 1 day. These data indicate, in accordance to literature on classical biofilms, that for the tested period, the algae-bacterial biofilm used for wastewater treatment is less sensitive to rotating speed and supports twice higher nutrient removals than the bacterial biofilm.

Methodology / Experimental approach

A laboratory multitrophic rotating biofilm contactor (MRBC) with a tank volume of 2.5 L was used in this study. Six PVC discs on which the biofilm grew were all identical with diameter of 10 cm and placed on the axle separated by two small rubber spacers of 1 cm. All discs have concentric grooves with dimensions (2x2 mm). The discs rotated at a relatively low speed (10 rpm) to avoid detachment events. Inoculation was carried out in batch mode for 7 days by mixing 800 mL of microalgae-bacterial flocs (MaB-flocs). After 7 days of anaerobic pre-culture of MaB-flocs, the feeding rate was maintained at 2.5 L.day⁻¹ of the synthetic wastewater during the anaerobic treatment. The concentration of the feeding solution was fixed to achieve 500 mg of COD.d⁻¹ 60 mg of NH₄⁺-N.L⁻¹ and 30 mg of PO₄³⁻-P.L⁻¹ under constant supply of light: dark cycles of 16:8h.

References

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Unnithan *et al*. (2014). Mini-review: a priori considerations for bacteria-algae interactions in algal biofuel systems receiving municipal wastewaters. *Algal Research*, 4, 35-40.

<p>2017</p> 	<p>Optimization of the microporous and its impact on aging and water management in fuel cell</p> <p>MARIEM BELHADJ (4th year)</p> <p>François Lapicque, Caroline Bonnet AXE 1 - SYSPOL</p>	
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General context, scientific issues

This thesis CEA-Tech is co-supervised by LRGP and Cea-Liten Grenoble with funding from Region Lorraine. The major challenge of PEMFC technology is to become a viable commercial vehicular power source with low emissions. PEMFC commercialization requires progress in terms of durability and cost effectiveness. Literature attention was focused on the membrane life time more than on the gas diffusion layer (GDL). The GDL is considered here a critical component since its degradation has an impact on the fuel cell durability.

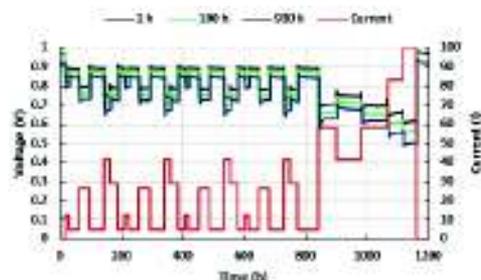
Objectives and stakes

The performance of PEMFC depends on the catalyst activity and the quality of its various components including the gas diffusion layer (GDL). In this study the impact of microporous layer (MPL), one part of the GDL, on ageing and water management in fuel cell is investigated. Because of water production in the cell, MPL hydrophobicity varies between the cell inlet and outlet. The challenge of this project is based on the understanding of ageing mechanism and the optimization of the diffusion medium¹ (MPL) to improve both PEMFC performance² and durability.

Methodology/ Experimental approach

The GDL design is based on electrochemical characterization and physical and chemical measurements. The degradation of new GDLs was performed under pressure according to the Fuel Cell Dynamic Load Cycle (FCDLC) comprising different variable load acceleration, full power and overload running conditions within an overall time period of 1200 s. The performance loss of the cell is investigated by various measurements made before and after NEDC cycling: i) Electrochemical tests such as polarization curves, electrochemical impedance spectroscopy (EIS), cyclic and linear voltammetry. ii) Physical and chemical measurements. Specific accelerated stress tests are carried out to identify the effect of GDL ex-situ ageing on electrochemical performance.

Illustration



Fuel cell response after 0 h, 100 h and 930 h during FCDCL, (one cycle's duration = 20 min), operating conditions ($\lambda_{H_2-\lambda_{air}} = 1.2-2$, RH= 50%, 1.5 bar, $T_{cell}=80^\circ C$)

Main results

The electrochemical measurements have been conducted in a 100 cm² fuel cell. The Membrane Electrode Assembly (MEA) with GDL and MPLayers were prepared in Cea-Liten. To evaluate GDL/MPL degradation, 500 cycles has to be performed. During the operation, gas flow rates are measured and controlled by a Dspace card[®]. This card was also programmed to collect all the data. The fuel cell current was measured during with an electrochemical charge connected to the Dspace card. Before the cycles, the fuel cell is conditioned at 1A/cm² at operating conditions. Throughout the first cycling, the cell response of MEA tested with homogeneous hydrophobicity distribution, showed a progressive decrease trend. The regularly voltage loss indicates the degradation of the GDL-MEA. Three operating conditions (dry membrane, humidified membrane and NEDC conditions) are performed in polarization curves to identify the effect of gas relative humidity and water content. EIS showed significant changes in diffusion resistance whereas ohmic resistance remained unchanged. The effects of cycling could also be observed from the regular decrease in Electrochemical Active Area. As a next step it is planned that some of the prepared GDL in assemblies exhibiting spatial distribution of hydrophobicity or different porosity gradient in view to optimal performance and durability in the cell.

References

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2017



Project: MEAClean

Marine Brogat¹ (Ingénieur de recherche)Cécile Vallières¹, Olivier Potier², Léa Sigot¹, Steve Pontvianne²,
Nicolas Mergenthaler³Axe 1 | SAFE¹ | SOLEO² | MEA France³

Keywords: surface runoff, rainwater, adsorption, cleaning system, metals, polycyclic aromatic hydrocarbons (PAHs)

General context, scientific issues

Urban runoff is a major cause of pollution and is the source of many pollutants which can affect the water quality and ecology of receiving waters. For example, motor vehicle emissions and vehicle tyre wear are some of diffuse sources of chemical contaminants in urban environments. During rainfall, these chemical contaminants are washed from different surfaces such as roofs and roads into the stormwater system [1, 2]. Heavy metals (copper (Cu), lead (Pb) and zinc (Zn)) and polycyclic aromatic hydrocarbons (PAHs) are of particular concern in such runoff due to their prevalence, toxicity to aquatic organisms and persistence in the environment [3, 4].

Main objective

The aim of this project is to test an innovative trench drain system with a multi-stage substrate technique to retain pollutants such as PAHs and heavy metals.

Methodology / Experimental approach

The study consists of different tests:

- Under monitored laboratory conditions, equilibrium adsorption (isotherm) studies will be carried out to evaluate the maximum capacity of the 2 substrates as adsorbents of PAHs and heavy metals in aqueous solutions using batch contact adsorption mode at different temperatures and pH. In fixed-bed column studies, the breakthrough curves will be studied at different operating conditions. Three metals (copper, zinc and lead) and three PAHs (phenanthren, pyrene and benzo[g,h,i]perylene) have been selected to carry out these laboratory experiments.
- Characterization of the 2 substrates will be realized to determine some parameters such as specific surface area.
- In pilot plant scale: a trench drain (with and without substrates) will be installed to follow global water quality parameters and retention of pollutants (heavy metals: copper, zinc, lead, nickel, tin, chrome and cadmium; organic pollutants: PAH16; hydrocarbons: hydrocarbon index) during one year under real conditions.

Illustration: Trench drain MEA®Clean Pro



- 1- Gratings
- 2- Retention basin for surface water
- 3- First layer of substrate : mineral mixture for the treatment of organically polluted rain (PAHs...)
- 4- Second layer of substrate : mineral mixture for the treatment of inorganic pollutants (heavy metals)
- 5- Third layer of substrate : mineral mixtures as an additional filter stage
- 6- Geotextile for retention of fines
- 7- Arched spacer to ensure a long-lasting clean channel section
- 8- Rigid channel body channel

First results and perspectives

At this moment:

- Different isotherm studies of heavy metals in single solution or in binary mixtures are underway at room temperature. The kinetics of adsorption are slow (several days).
- Metal quantification for samples under laboratory conditions and under real conditions is carried out by inductively coupled plasma – optical emission spectrometry (ICP-OES) and by inductively coupled plasma–mass spectrometry (ICP-MS), respectively.
- Determination of specific surface area of substrates using BET method is ongoing.

- Reflections on the implementation of the pilot plant (choice of water sampling systems,...). The public works will take place during this summer on the LRGPs car park.

Perspectives:

- Different isotherm studies of heavy metals and PAHs in single solution or in binary mixtures will be realized.
- PAHs quantification for samples under laboratory conditions and under real conditions will be carried out by gas chromatography – mass spectrometry (GC-MS).
- After implementation of the pilot plant, trench drain will be studied under real conditions.

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2017 	Recovery of rare earths from hyperaccumulator plants <u>Zeinab CHOUR (2nd year)</u> Laurence Muhr, Baptiste Laubie Axe 1 SOLEO	
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Keywords: Rare earth elements, hydrometallurgy, extraction agent, biomass, cationic resin

General Context, scientific issues
 The rare earth elements (REE), which comprise 15 lanthanides and yttrium with similar chemical and geochemical properties, make up a special group of heavy metals in the research fields of plant nutrition and environmental toxicology. [1]
 They have become increasingly important in the transition to a more sustainable, low carbon economy, because of their essential role in permanent magnets, lamp phosphors, rechargeable NiMH batteries, catalysts and other industrial applications...
 Phytoremediation, defined as the use of plant to remove, immobilize or degrade contaminants, is thought to be a feasible way to decrease the harmful effects of metals in soil and has a great potential for in-situ and low-cost remediation [2]. REEs can be extracted by hyper-accumulator plants and current studies focus on REEs recovery from plants to recycle it.

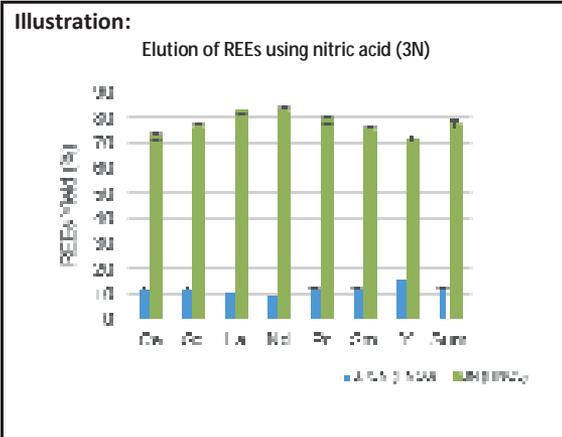
- Objectives and stakes**
- Characterization of biomass
 - Process design for REEs recovery
 - Separation of major REEs

Methodology / Experimental approach
 Hyperaccumulator plant used is *Dicranopteris Dichotomas* which has a very strong ability to accumulate REEs.
Following approach is adopted:
 Determining of the composition of the biomass with digestion

2 ways of rare earth element recovery are assessed:
 -Direct extraction using EDTA followed by selective precipitation using oxalic acid.

-Extraction in acid solution and cationic resin, followed by elution steps using nitric acid

Elementary composition of biomass is determined by ICP-AES after digestion step (HNO₃/H₂O₂). Solid particles are analyzed by XRD.



Main results
Dicranopteris dichotomas contains between **2000 and 4000 mg/Kg** of REE, in majority La, Nd and Ce. Plants also contain other compounds such as Al, Ca, K, Mg, Mn and also S and P.

Biomass leaching with EDTA leads to extract more than **80% of REEs** present in plant. Then, selective precipitation carried out leads to precipitate more than **70% of REEs** with purity more than **90%**.

Biomass leaching with cationic resin, in nitric acid allows us to extract **80% of REEs**. Elution steps using nitric acid leads to eliminate impurities and obtain a solution of REEs with purity more than **80%**.

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<p>2017</p> 	<p>Experimental study and modeling of hybrid solid/solid explosions: an application to mixtures of graphite/metal dusts</p> <p>Miriam D'Amico (3rd year)</p> <p>Olivier Dufaud, Jean-Claude Latché</p> <p>Axe 1 IRSN</p>	
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Keywords: dust explosion, hybrid mixtures, severity, turbulence, flame propagation

General context, scientific issues

The UNGG reactors (Natural Uranium Graphite Gas) were the first generation of nuclear power reactors in France. The last reactor of this type has been shut down in 1994. The possibility to encounter dusts composed of graphite and metals particles, during decommissioning activities or stored in silos, has led to characterize their flammability and severity properties to support the future safety analyses of decommissioning operations. Actually, a safe decommissioning is a lengthy process that requires careful planning, close attention to technical details and a complete risk assessment of the plant [1].

Illustration: Experimental setting used to study the dust dispersion phenomenon in the 20-liters sphere.



Objectives and stakes

The objectives of my PhD work are on the one hand to better understand the explosive phenomenon of such mixtures by means of an extensive experimental work and on the other hand to model it by developing a programming code that can be extended later to binary mixtures of dust graphite / metal (magnesium and / or iron).

Main results

The modification of graphite dusts explosivity strongly depends on the nature of the metal considered. On the one hand, 30% wt. of iron dust markedly promotes the ignition phenomenon in layer causing a decrease of roughly 53% of the graphite minimum ignition temperature. On the other hand, the same amount of magnesium powder does not induce a noticeable change. These different behaviors are particularly related to the oxide layer coverage and the oxygen accessibility in the storages.

Methodology / Experimental approach

The sensitivity to self-heating and ignition and the severity to explosion of such mixtures have been assessed in a standardized way in order to estimate the minimum ignition temperature in dust layer and cloud, the minimum ignition energy, the maximum explosion pressure and the deflagration index. The flame stretching and propagation have been observed with a high speed camera in a vertical squared tube, coming up with the estimation of a pseudo laminar flame velocity by using an approach similar to the one developed for pure gases [2]. Moreover, the time evolution of turbulence intensity and mean particle velocity resulting from the dust dispersion in the 20-liters explosion sphere have been studied by implementing the Particle Image Velocimetry technique (PIV see illustration). Such experiments have been completed by in situ laser granulometry analysis, the severity being strongly dependent on the spatial dust size distribution at the time of ignition. Experimental results have contributed to develop a numerical model predicting the severity of graphite in a confined space based on the description of the flame structure and the analysis of the resulting temperature, velocity and concentration fields.

A parametric study has also been realized to investigate how the explosivity depends on several parameters (initial turbulence, ignition energy, particle size, dust humidity, etc.). Turbulence plays an important role in the cloud uniformity and in the local variations in dust concentration, which impacts in turns the mixture explosivity. The velocity field resulting from the dust injection in the explosion sphere has been characterized, as well as the time evolution of the turbulence intensity. A significant decay has been observed from 80 ms and a stabilization phase to begin at roughly 160-180 ms.

Because of the presence of metals in the mixture, the possibility of hydrogen production resulting from the reaction with water vapor at high temperatures could not be neglected. It leads to an enhancement in the severity, when the relative humidity slightly increases.

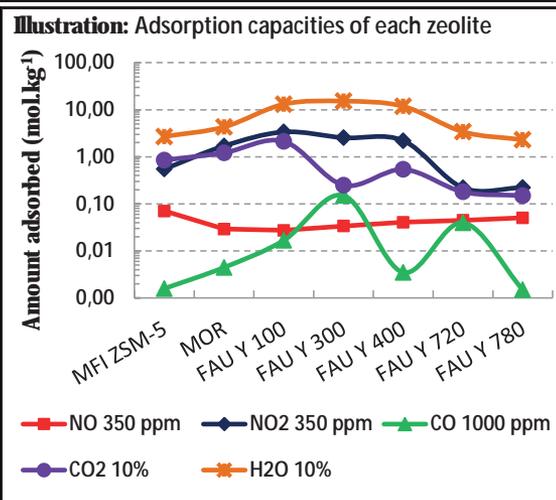
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2017 	Study of the feasibility of a gas-solid adsorbent for treatment of NO_x and CO in the presence of water Applications to diesel engine exhaust emissions in confined spaces Florine Delachaux (2nd year) Cécile Vallières (LRGP), Hubert Monnier (INRS) Axe 1 SAFE	
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Keywords:
 gas-solid adsorption, NO_x, CO, H₂O, diesel exhaust, zeolite

General context, scientific issues
 In France, about 800 000 employees are potentially exposed to diesel exhaust emissions by working in confined spaces like in automotive garages or during the construction and maintenance of tunnels for example. The aim of this project is to remove nitrogen oxides (NO_x: NO and NO₂) and carbon monoxide (CO) from the exhaust gas of these vehicles. One of the solutions is to use an adsorption process. The main scientific lock is the temperature of the exhaust gas which is unfavorable to the process. The presence of other components such as carbon dioxide (CO₂) and water vapor (H₂O) is also a critical point which can lower the performance of the developed process.



Objectives and stakes
 The steps to perform the study are:

- Select some adsorbents able to capture NO_x and CO
- Test these adsorbents with NO, NO₂, CO, CO₂ and H₂O to find the more efficient
- Find the best configuration in order to obtain an effective system

Main results
 On the above illustration, the chosen concentrations are representative of the average concentration of the compounds in diesel exhaust gas. The goal is to select zeolites which can adsorb high level of NO_x and CO but low level of CO₂ and H₂O.
 In terms of adsorption capacity, two zeolites adsorb more CO than the others: these zeolites are faujasites FAU Y 300 and 720.
 As regards NO adsorption capacities, they are equivalent for all of the zeolites studied.
 For NO₂, three zeolites stand out from the others: FAU Y 100, 300 and 400. It would seem that the better adsorption of NO₂ is therefore mainly due to the low Si/Al ratio of these adsorbents.
 Zeolites which adsorb simultaneously less CO₂ and less H₂O than the others are FAU Y 720 and 780 which are both composed with H⁺ cation.
 The results on the pure substances made it possible to select three faujasites: FAU Y 300, 720 and 780.

 On these zeolites, multi-components (NO / NO₂ / CO) breakthrough fronts will be measured in the presence of oxygen and water vapor and at higher temperatures. After that, real conditions could be tested on the best adsorbent.

Methodology / Experimental approach
 After selecting seven zeolites according to the literature, the physical structure (surface area and pore size distribution) were obtained by physical adsorption. Adsorption capacities of each zeolite depend on the structure, on the Si/Al ratio and on the charge-compensating cation. Pure components adsorption permitted to show the influence of these parameters. For adsorption of NO and NO₂, breakthrough curves were performed whereas isotherms were achieved for CO, CO₂ and H₂O. Isotherms obtained have been modelled with Langmuir, Sips and Toth models. Langmuir best describes the experimental data. Thanks to these results at ambient temperature, three zeolites were selected.
 The next steps will be to determine the capacity and the kinetics of transfer when mixture of gases is in contact with adsorbent at different temperatures. In the final step, the shape of the adsorbent will be optimized to get an effective system.

<p>2017</p> 	<p>PhD subject : Depollution of waters by electro-coagulation process: Application in Zn and Fe containing water potabilisation</p> <p style="text-align: center;"><u>Amira DOGGAZ</u></p> <p style="text-align: center;">François LAPICQUE, Marie LE PAGE MOSTEFA Axe 1 SYSPOL</p>	
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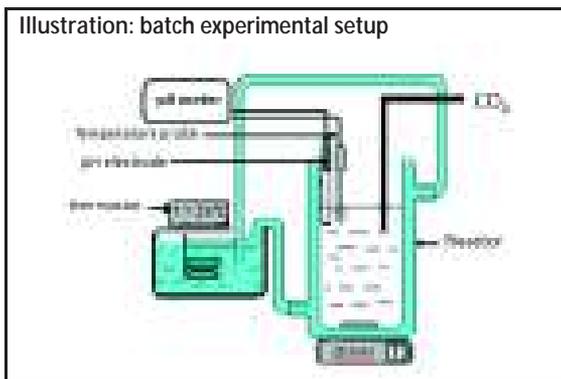
Keywords: Electro-coagulation, iron, oxidation, precipitation, adsorption

General context, scientific issues
Iron is one of the most common elements in nature. It can be found in fresh waters at a concentration of 0.5-50 mg/L. Although the moderate toxicity, iron can cause many industrial and aesthetic problems. Hence, the OMS limits the concentration of iron in drinking water to 0.3 mg/L. Electrocoagulation is a promising technology for iron removal from waters. This method involves various phenomena: adsorption of Fe^{2+} on $Al(OH)_3$, precipitation of $Fe(OH)_2$ at the vicinity of the cathode where the pH is higher, oxidation of Fe^{2+} to Fe^{3+} followed by precipitation of $Fe(OH)_3$ [1]. This oxidation-precipitation is affected by the presence of ions (such as chloride and sulfate ions) and $Al(OH)_3$ flocs.

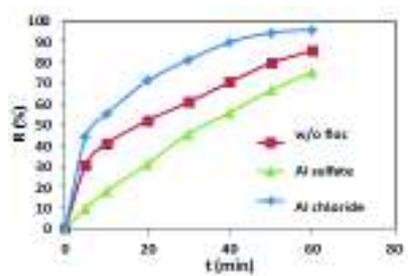
Objectives and stakes
The aims of this research are:
- to study the effect of chloride and sulfate ions on iron removal by oxidation-precipitation.
- to evaluate the role of $Al(OH)_3$ on iron removal in oxygenous and anoxic conditions.

Methodology / Experimental approach
Fe (II) oxidation tests were carried out in a glass vessel thermostatically controlled. Amounts of NaCl or Na_2SO_4 are added in 1 L deionized water under stirring rate of 400 rpm. The pH was adjusted to 6.5 using CO_2 -bicarbonate buffer system. At $t=0$, a dose of ferric sulfate (25 mg/L as Fe^{2+}) is introduced to the solution. At various time intervals small volumes of the solution were withdrawn and filtered immediately by a 0.45 μm pore size membrane filter. For oxidation tests in presence of coagulant, $Al(OH)_3$ is formed by adding Al chloride or Al sulfate and 3 M NaOH solution slowly until desired pH was reached.
In adsorption tests, purified N_2 was bubbled through the $NaHCO_3$ solution containing $Al(OH)_3$ preformed. This removed O_2 almost completely from solution.

All experiments were conducted at constant temperature ($T=25^\circ C$) and samples were analysed for Fe^{2+} by 1,10-phenanthroline method (Rodier 1996).



Main results
Effect of $Al(OH)_3$ on Fe(II) removal



- Sulfate and chloride ions were shown to hinder the Fe(II) oxidation to Fe(III). This is attributed to ion-pairs formation: $FeCl^+$ and $FeSO_4^0$ [2].
- $Al(OH)_3$ enhances the Fe(II) oxidation-precipitation. This role prevails on the presence of chloride, but not for sulfate anions. This can be explained by the stronger inhibiting effect of sulfate ions in comparison with chloride ions.
- In anoxic conditions, Fe^{2+} ions are adsorbed on $Al(OH)_3$ flocs. Removal efficiency does not exceed 20% for molar ratio $Al/Fe = 22$ at $pH = 6.5$.

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<p>2017</p> 	<p>Project : Development of an artificial wetland in Reims for Reclaimed water polishing and stormwater treatment</p> <p><u>Maïa DUROZIER</u> (engineer) Supervisor Marie-Noëlle PONS Axe 1 SOLEO</p>	
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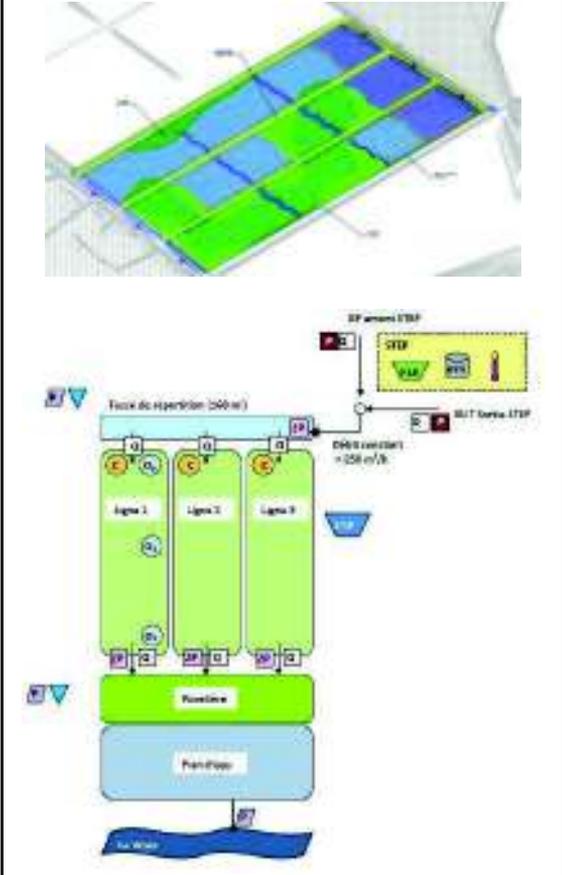
Keywords: artificial wetland, downstream of a wastewater treatment plant, treatment of rainwaters, phytoremediation, pollutants, monitoring, physical and chemical sensors, chemical analysis

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. In addition, these wetlands could be a solution for treating urban wastewater by-passed during rainy events.

Objectives and stakes
The construction of wetlands to polish the treatment of treated waters is already used in France, but it mainly concerns small wastewater treatment plants. The aim of AZHUREV project is to build a large-scale demonstration wetland downstream of the Reims Métropole wastewater treatment plant (more than 210 000 inhabitants) to provide an improved treatment during dry weather and a treatment of by-passed stormwaters. At the same time, this project wishes create habitats for wetland biodiversity. My aim is to monitor the system and its performance in terms of abatement of primary pollution and of some micropollutants for dry and rainy weather and to understand the abatement mechanisms.

Methodology / Experimental approach
The wetland is composed of three ponds (350m long and 50m wide), 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 station output water supply is stopped and the ponds are supplied by urban rainwater. At the exit of the ponds, the water passes through a reed bed and a lake before being discharged into a canal that flows downstream into the Vesle River. Flow meters, temperature and conductivity sensors will be installed continuously at the entrance and exit of each pond. A meteorological station will be installed. The wetland functioning will be monitored during 1 year. Using automatic samplers, a sampling campaign will be conducted monthly for dry weather. Additional sampling campaigns will be organized during the large rain events. With an aquatic drone, samples will be collected in the ponds, the lake and the dissolved oxygen will be measured all along the ponds.

Illustration: Wetland configuration and monitoring scheme



Main results
The construction of the artificial wetland is just finished. The water supply of the three ponds is expected in June 2017. The first campaigns are programmed in summer 2017. The initial state of the lake is currently investigated.

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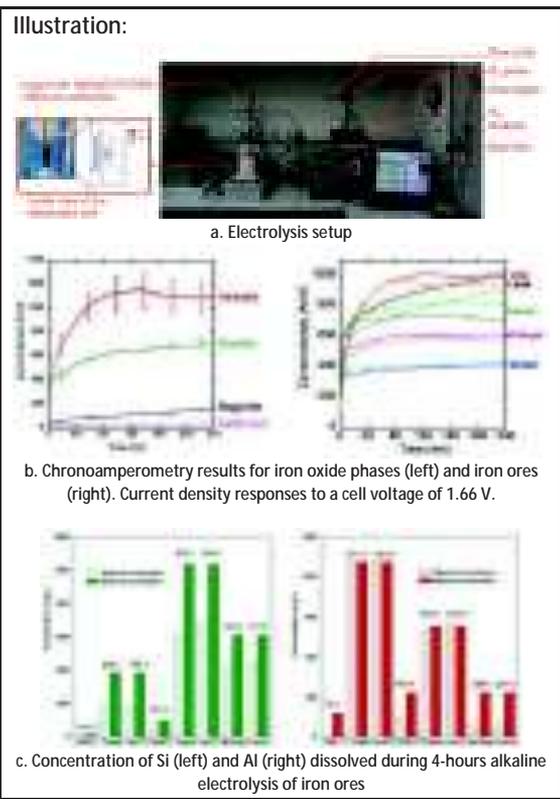
<p>2017</p> 	<p>Effect of gangue removal from Iron ore by alkaline leaching on its reduction into Iron through Alkaline Electrolysis</p> <p>Vincent Feynerol (3rd year)</p> <p>Marie-Noëlle Pons, François Lapicque Axe 1 SOLEO - SYSPOL ArcelorMittal</p>	
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Keywords: Alkaline Leaching ; Alkaline Electrolysis ; ULCOWIN Process ; Iron Oxides ; Gangue ; Siliceous Phases ; Aluminous Phases ; Sodium Hydroxide ; Kinetics ; Thermodynamics

General context, scientific issues
 In order to reduce steelmaking CO₂ emissions, ironmaking by low temperature alkaline electrolysis has been investigated during last decades. Although iron production from pure hematite electrolysis is efficiently achieved, substitution of hematite with iron ore in the process results in a significant drop in faradaic yield. One or several compounds in the gangue therefore seem to have a detrimental effect on the electrochemical reduction of iron ore. These compounds must therefore be identified and removed by a purification step prior to the electrolysis.

- Objectives and stakes**
- Find out if purification of iron ore by alkaline leaching can efficiently be achieved
 - Verify if this purification has a significant positive effect on the faradaic efficiency of iron ore electrolysis
 - Use thermodynamics to validate experimental results
 - Consider the feasibility of this process at a larger scale

Methodology / Experimental approach
 Gangue compounds, mostly siliceous and aluminous phases, can be selectively dissolved by sodium hydroxide through alkaline leaching. In order to better understand the kinetic behaviors of these compounds during alkaline leaching, an experimental setup was built. This setup will allow quick introduction of pulverulent ore in hot leachant as well as in situ sampling during the reaction plus acquisition of multiple parameters: pH, temperature, humidity and electrochemical potential. On another hand, an electrolysis apparatus was built so to test the electrochemical reactivity of treated iron ore. This setup was used to compare the reactivity of the most common iron oxide phases (hematite, goethite and magnetite) by comparing current density responses to a same constant cell voltage. This setup was also used to compare the reactivity of several iron ores with different beneficiation degrees to determine which of the gangue compounds are the most deleterious.

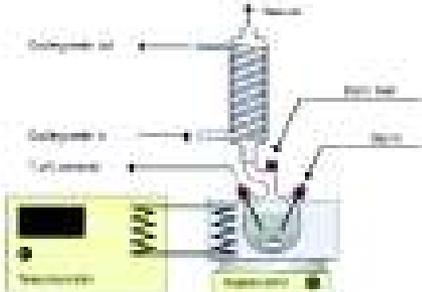


- Main results**
- Chronoamperometry experiments conducted on hematite, magnetite and goethite showed that hematite is the most reactive iron oxide phase
 - Chronoamperometry experiments conducted on different iron ores showed that silicon has a very small effect on the process efficiency compared to aluminum and magnetite.
 - Gibbsite, kaolinite and quartz readily dissolve into 50% NaOH at 110°C after a 6-hours leaching.

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<p>2017</p> 	<p>Mineral CO₂ carbonation process beneficiation: separation and recovery of co-products</p> <p><u>Karine Gerardin (Contract research engineer)</u> François Lapicque, Hervé Muhr Axe 1 SysPol (Polyphasic System)/EMMAD (Divided material development) Keywords : carbonation, leaching, olivine, beneficiation, silica</p>	
<p>General context and objectives</p> <p>Because of the increasing use of the fossil fuels, since the end of 1950s, the content in CO₂ have not stop growing. This growth generates deep concerns as for their impact on the ground ecosystems today. The reduction of CO₂ emissions is thus an important stake which requires to associate at the same time several behavioural and technological solutions. Capture and storage of CO₂ is an envisaged solution which would allow to reduce its emissions towards the atmosphere. This technology supposes to trap the CO₂ produced by the big industrial emission places, to transport it then to store it durably in the geologic environment. So, the mineral storage ex-situ of the CO₂ in the olivine proposed in this study calls on to the process of carbonation that is in the formation of mineral phases (carbonates) trapping the carbon. The formation of carbonates establishes a long-lasting option of geologic detention of the carbon dioxide, susceptible to participate significantly in the reduction of the emissions of anthropogenic origin. However, these methods of capture have a cost that it is necessary to balance via the beneficiation of co-product. In this part of VALORCO project, this action of beneficiation is mainly studied here.</p>		<p>Principle and protocol</p> <p>The first mechanism stage of reaction consists in acid leaching of silicates resulting in the precipitation of silica recovered by pressurized filtration and in the extraction of the cations, Mg²⁺ or Fe²⁺ and Ni²⁺ in solution. The second stage consists of the precipitation of carbonates in the presence of dissolved CO₂ from the previous solution. In this paper we mainly consider the first stage.</p> <p>The acid leaching is achieved with stirring under inert atmosphere at temperature between 80 to 100°C. Experimental time varies from 1h30 to 3h00. Two different low cost acids (H₂SO₄ and HCl) were tested at various concentration and with a high solid area and solution volume ratio. After acid dissolution the experimental medium is neutralized at a pH higher than 2 then filtered and washed. The recovered silica is dried and then characterized by microscopic observations and density, granulometry, specific area, humidity measurements. Concentrations of solutions are determined by ICP-MS method.</p>
<p>Material and method</p> <p>The raw material used (reference Olivine Green Lightning® GL30) is a standard industrial ore rich in magnesium silicate and extracted of dunite produced by the Group SIBELCO of size grading 0,063-0,125 mm with constant properties. The leaching device is presented in figure 1.</p>  <p>Figure 1: Leaching device</p>		<p>Main results</p> <p>The results of the first phase of this study show that:</p> <ul style="list-style-type: none"> • Increasing temperature from 80 to 100 ° C has a favorable influence on the dissolution efficiency, which increases by 50 to 60%. This, however, also increases the overall energy cost of the process. • Whatever the nature of the acid used, the dissolution yield is similar. In order to limit the cost of neutralization, future experiments will have to optimize the amount of added acid. • Olivine ultrasonic pretreatment does not significantly influence the rate of dissolution. • Dissolution by H₂SO₄ under N₂ with neutralization between 2 <pH <3 results in almost white solid compounds and colorless solutions (absence of Fe oxidation) whereas in the same condition, dissolution by HCl results in brownish solid compounds (presence of iron III) and green filtrates (iron sulfate II). • The characterizations carried out by the SEM and supplemented by semi - quantitative analyses by EDS show that the white washed and dried solid compound consists mainly of silicium and oxygen. <p>Further characterizations are currently in progress</p>

<p>2017</p> 	<p>PhD subject : Biphasic Aerosols Filtration ☐ Solids Agglomerates and Liquids Droplets (Falbala)</p> <p>Charlotte Godoy (1st Year)</p> <p>Dominique Thomas, Augustin Charvet Axe 1 SAFE</p>	
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Keywords: Filtration, Soot particles, Droplets, Biphasic aerosols, Fibrous filter

General context, scientific issues

Fibrous media embody the most effective and widely used method for separating ultrafine particles from a carrier fluid. This separation technique, used for the protection of people and environment, is proven in terms of initial collection efficiency but its behaviour over time remains difficult to predict.

This observation is all the more noticeable when these devices are exposed to biphasic aerosols constituted by solid and liquid particles. These situations can notably occur during metals machining, pesticides spreading or even during fire in confined zones such as nuclear power plants.

Objectives and stakes

The aim of this study is to examine the performances of a fibrous media towards biphasic aerosols constituted by solid particles (micron-sized or nanostructured) and of droplets (submicron-sized or micron-sized).

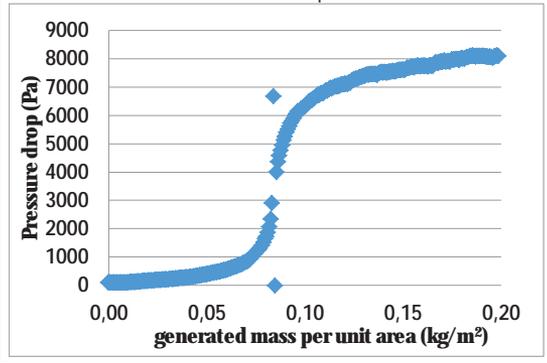
If the filtration of solid or liquid aerosols is relatively well documented in the literature, no study has been interested in the collect of diphasic aerosols.

Methodology / Experimental approach

This thesis work is divided into four steps:

- A bibliographic report structured around four main axes: Solid aerosols filtration, liquid aerosols filtration, solid aerosols filtration under humidity and biphasic aerosols filtration.
- The setting up of two separate experimental benches: one to characterize the soot generation of the mini-CAST (Combustion Aerosol Standard) and the other one to characterise a water droplet generator.
- The development of a small-scale experimental bench for the study of biphasic aerosols filtration. The development and validation of the protocol to characterise the particle size of such aerosol.
- Performing biphasic aerosol filtration tests of pleated filters on the CATFISH test bench (Analytical Characterization of Filtration under Moisture).

Illustration: Evolution of the pressure drop for a HEPA filter with droplets water



Main results

Two experimental benches have been established: one with a generation of water droplets and another with soot particles from the CAST generator. The aim of these two benches is to characterize the two generation (water and soot) separately before mixing them.

The size distribution of the water aerosols could be obtained with an optic counter (Welas 2000 H). The results show a monodisperse distribution with a median diameter around 0,360 µm.

A loading of high efficiency filters has been made with water droplets and soot particles separately. The illustration shows one of the results for the loading of HEPA filter by droplets water. This evolution of the pressure drop with the generated mass per unit area is characteristic of liquid aerosol filtration. Indeed, there are three steps: a slow increase of the pressure drop, then an exponential rise, at the end a stabilisation is obtained and drainage of the liquid appears. Concerning, the soot particles, the loading is also characteristic of solid aerosol filtration. The loading of HEPA filter with soot particles has been tested with different air/fuel ratio.

2017 	Design of innovative processes to produce nickel and cobalt carboxylates after metal extraction from secondary resources by hyperaccumulator plants <u>Mathilde Guilpain (2nd year)</u> Marie-Odile Simonnot, Baptiste Laubie Axe 1 SOLEO	
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Keywords: hydrometallurgy, separation engineering, extraction, biomass

General context, scientific issues

The world has to face new challenges regarding metal resources and recycling. In this context, new secondary resources have to be considered. Some of them are wastelands and industrial wastes, which contain significant amounts of heavy metals but not enough to be treated by traditional pyrometallurgy or hydrometallurgy. Agromining is a new approach, based on hyperaccumulator plants (HA) [1]. These plants have the capacity to extract metals from soils and to accumulate them in their tissues at high concentration (e.g. over 1000 mg/kg of dry plants for nickel and cobalt). Once the best candidates of HA are selected to extract nickel and cobalt, my study consists of developing methods to produce nickel and cobalt carboxylates, given that Ni and Co are chelated to carboxylates in the plant tissues [2]. This work is part of the ANR program Agromine [3].

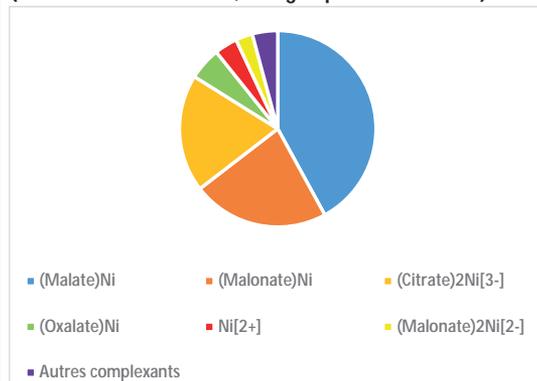
Objectives and stakes

- Produce nickel carboxylates from *Alyssum murale* (HA grown in the Balkans) in mild conditions.
- Test and adapt the process developed on *Rinorea bengalensis* (tropical HA tree grown in Malaysia).
- Produce cobalt carboxylates from cobalt HA (*Berkheya coddii*) in mild conditions

Methodology / Experimental approach

To preserve organic matter, Ni is extracted from the dry plants by water using a packed bed column. The extracts are characterized by ICP-AES to measure metal contents, by HPLC to identify and quantify the organic acids extracted and by ionic chromatography to analyze sugars. Using all these data, Ni speciation has been determined using Jchess software (calculation of chemical equilibria). Then, different methods are tested to recover Ni from the extracts: sulfide precipitation, concentration by elimination of the others cations using decanoate and ion exchange with a chelating resin. A comparable approach will be followed with Co HA.

Illustration: Nickel speciation in the extracts (calculated with JChess, using experimental data)



Main results

- 80% of nickel is extracted from the dry plant *Alyssum murale* using water in a packed bed column ([Ni] = 10 mM).
- Extracts also contain K (25 mM), Mg (9 mM) and Ca (8 mM), anions, as well as high diversity of organic compounds.
- Ni is complexed by different carboxylic acids, mainly malate (42%) and only 5% of Ni is free.
- During sulfide precipitation, organic matter impacts germs growth and fosters nucleation, leading to the formation of tiny particles which cannot be filtered.
- Decanoate precipitation did not enable us to isolate Ni, since Mg could not be separated from the extract.
- The results obtained with the chelating resin are very promising. Ni carboxylate could be isolated. Work is in progress to find optimal operating conditions.

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<p>2017</p> 	<p>PhD subject: Removal of micropollutants in wastewater treatment plants; effect of hydrodynamics configuration of the biological reactor on the elimination of micropollutants</p> <p><u>Rana Hatoum</u></p> <p>Olivier Potier, Harald Horn, Joumana Toufaily Axe 1 SOLEO</p>	
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Keywords: micropollutants, hydrodynamics, biological reactor, activated sludge

General context, scientific issues

The majority of wastewater treatment plants (WWTPs) have not been designed to treat micropollutants. Until now, they are capable of removing suspended solids, carbon, nitrogen and more or less phosphorus. They are considered to be one of the main emitters of micropollutants to aquatic environments. Several biodegradable micropollutants, are not degraded in the biological reactors of sewage treatment plants, and found at the outlet of treatment plants.

Objectives and stakes

The main objective of this study aims at improving the purification of the biodegradable micropollutants, but poorly degraded in biological treatment plants. The principle of this work is based on the Approaches of Chemical Reaction Engineering which combine hydrodynamic and kinetic aspects. The reactions whose kinetics depend on the concentrations can be intensified by using the adapted hydrodynamics, which look for optimum forms of reactor.

Methodology / Experimental approach

This work is carried out in several stages on two sites in France and Germany : LRGP in Nancy and KIT in Karlsruhe.

- First part: (1st year) Already realized

A bibliographic study was carried out on the different types of micropollutants more or less biodegradable. In agreement with KIT's team and from bibliography information, five micropollutants were selected, depending on several factors: issues, biodegradability, possibilities for being analyzed in KIT's lab. A simulation of micropollutants degradation was initiated for simple hydrodynamics.

- Second part:

Experiments will be carried out to study the kinetics of degradation of micropollutants and the influence of local parameters on this process. This part will be made in Germany on a period of 5 months. The 5 micropollutants will be tested on a special laboratory pilot that allows to determine precise micropollutant removal kinetics in a lot of conditions.

- The third part will be completed within the LRGP laboratory in order to test different hydrodynamic configurations, which should make it possible to increase the purification yields.

Illustration: Wastewater treatment plant



Main results

The PhD started on middle of November 2016.

First results from simple systemic simulation were obtained. They show reactor hydrodynamics could have an impact on micropollutants removal up to 25% (the input concentrations ranging from 10^{-5} g/m³ to 10^{-3} g/m³).

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<p>2017</p> 	<p>Energy recovery from nickel hyperaccumulator plants</p> <p>Claire Hazotte (Post-doc) M.O. Simonnot, B.Laubie Axe 1 SOLEO</p>	
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Keywords: hyperaccumulator plants, agromining, combustion, energy

General context, scientific issues
 Within the SOLEO team, a strong expertise has been developed in the recovery of metals from hyperaccumulator plants, particularly for nickel [1, 2, 3]. In most cases, the 1st step of the process is combustion [4] of dry plants that generates energy, gases and fumes. This work aims at investigating this step, to evaluate the possible energy recovery.
 This work takes place in the European project Agronickel (FACCE Surplus program), aiming at providing new research to transform already existing agromining into a fully green technology at implementation stage.

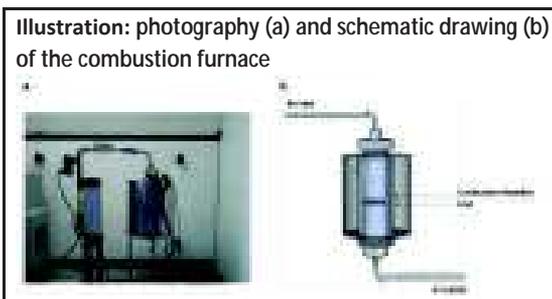
Objectives and stakes
 The main objectives of this work are:

- to determine the calorific value of the different Ni hyperaccumulator plants,
- to characterize the gaseous emissions from the plants combustion,
- to study energy recovery at pilot scale with a biomass boiler.

Methodology / Experimental approach
 Three nickel hyperaccumulator plants have been studied: *A. murale*, *L. emarginata* and *B. coddii*. The first experiments consisted of plant characterization: chemical composition (metals, CHONS concentrations) and physical properties (ATG, density and moisture). Then, the calorific values were determined:

- by correlations with CHONS composition
- by calorimeter experiments in a static bomb calorimeter, a sealed Parr 5100.

Finally, gaseous emissions were characterized, using a modified Godbert Greenwald furnace, in partnership with SAFE team. In this oven, the crushed plants are dispersed into an open vertical tube and heated at 550 and 900 °C under air gas. A grid has been added inside the tube to maintain the biomass for a total combustion. The oven is represented by a photo and a schematic drawing in Illustration. Gases were analyzed with a four-way micro gas chromatography: H₂, CO, CO₂, N₂, C₂H₄, C₂H₆, C₂H₂, C₃H₆, O₂ and CH₄.



Main results
 All the plants have comparable concentrations of C ($\approx 43\%$), H ($\approx 5.5\%$), O ($\approx 40\%$), N ($\approx 1.5\%$) and S ($\approx 0.5\%$), a density of 1.4 g cm^{-3} and water content between 5 and 9%. Thermogravimetric analyses have shown that the successive mass losses against temperature corresponded to water vaporization, degradation of cellulose, hemicellulose and lignin. At 550 °C, the obtained ash weight reaches 8% of the initial weight and 5% at 900 °C, allowing for the concentration of Ni by a factor of 20. No metal loss was recorded during temperature increase. Experimental and calculated gross calorific values are consistent, reaching $ca\ 17\text{ MJ kg}^{-1}$ of dry biomass, which are a little lower than recorded values for wood (20 MJ kg^{-1}).
 At 550 °C, the main gases were CO₂ and N₂ and at 900 °C, the combustion of plant emits CO₂, CO, H₂ and N₂ with the order of magnitude.
 These first results are very promising, since no metal vaporization was recorded, while energy production was high, which opens perspectives for recovery.

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<p>2017</p>  	<p><u>Innovative and continuous production of monoclonal antibodies with sequential multicolumn chromatography</u></p> <p><u>Nicolas-Julian Hilbold (3rd year)</u></p> <p>Laurence Muhr AXE 1 SOLEO Novasep Process SAS Merck KGaA</p>	
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Keywords: Monoclonal antibodies, continuous processing, multi-column chromatography

General context, scientific issues
 With 35% volume of marketed therapeutic proteins, monoclonal antibodies (mAbs) are today one of the most important drugs developed for human use[1]. The advances in cell culture over the last decades led to important improvements in production yields, displacing the capacity bottleneck towards purification steps, mostly operated in batch mode. Chromatography remains the main workhorse of mAbs purification, with typically 2-4 chromatography steps[2]. Operating chromatography in batch mode in industry usually implies a sub-utilization of resins resulting in low productivity and high buffer consumption, as well as requiring large and expensive equipment. Among other alternatives, Sequential multicolumn chromatography (SMCC) has been developed to overcome these issues and identified as a serious solution[3]. The proof-of-concept has been recently demonstrated[4] and the next step is its integration and implementation at industrial-scale.

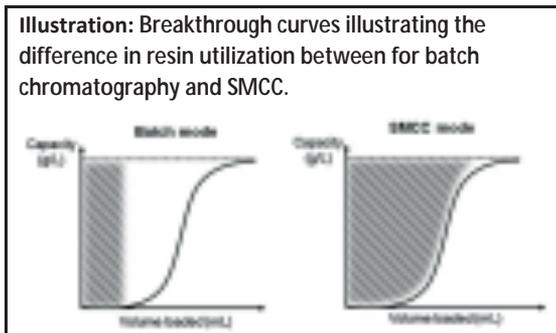
Objectives and stakes
 Develop an, industrial optimized sequential chromatography process based on the SMCC technology for the purification of mAbs

If necessary, design a new equipment meeting the specifications highlighted by the previous steps

Methodology / Experimental approach
 Gain knowledge on the SMCC process and continuous chromatography in general by:

- Characterizing batch chromatography system
- Using a modelling model and an objective-driven simulation tool to generate SMCC recipes
- Applying these recipes on the SMCC equipment and generate quantitative and qualitative data
- Select the most suitable development strategy and optimize the SMCC process for mAb purification

Perform scale-up and possibly integrate the SMCC step within a typical mAb production process.



Main results
 So far, an equipment to perform SMCC processes has been developed and built. Previous research works established a representative mathematical model and a computational-based optimization approach. A proof-of-concept has also been performed. This new research work began in February 2015 and is still at the early stage. However, expected outcomes of this research work include:

- Development of an optimized process for mAb purification
- Confirmation and rational understanding of the gains (productivity, operational expenses, etc.) expected from SMCC compared to batch chromatography,
- Demonstration of the robustness of the SMCC process and equipment,
- Increase the process knowledge of continuous chromatography and continuous processing in general

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2017	Flow field investigation of high solid anaerobic digestion by Particle Image Velocimetry (PIV)	
	<u>Yuying HU (3rd year)</u> Huai-Zhi LI, Souhila PONCIN, Jing WU Axe 1 SysPol	

Keywords: HSAD; Flow fields; Non-Newtonian fluid; PIV; Rheological behavior

General context, scientific issues

High solid anaerobic digestion (HSAD) is a promising technology for its small reactor, low heating energy and small digestate generation. However, high viscosity of HSAD's digestate leads to difficulties in homogenization and mixing [1]. Flow fields describe straightforwardly the dynamical efficiency of homogenization. Thus, the investigation on HSAD's flow field is essential.

Objectives and stakes

The present work aims at gaining insight into the flow fields inside a complex HSAD reactor, as well as exploring a new approach for measuring the flow field in the opaque media.

Methodology / Experimental approach

Rheological characteristics of HSAD's digestate and the working fluids (i.e. 1.00% (wt) PAAm solution and 3.00% (wt) laponite suspension) were measured on a Rheometer (AR-G2, TA, USA). Then, we used the PAAm solution as intermediate case, and the laponite suspension as the simulant of HSAD digestate.

PIV system was used in this study. Silvered glass microspheres were used as seeding particles, their sedimentation could be neglected under our agitation [2]. The laser beam was produced across a cylindrical lens, and was focused on the plane of the reactor's vertical symmetry axis.

The experimental set-up is illustrated in Fig. 1(a). The impeller (Fig. 1(b)) used in this study was printed via a 3D printer. It was derived from the standard C200 impeller, and its diameter was 50 mm.

(a) (b)

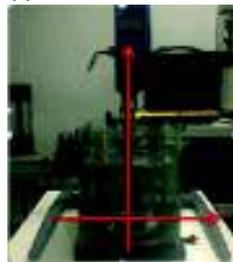
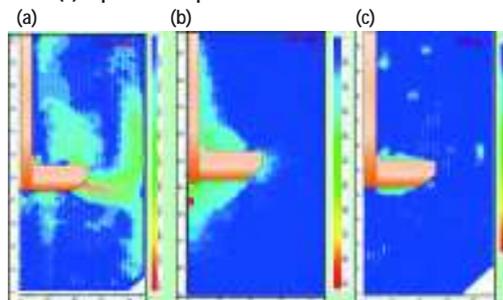


Fig. 1 Diagram of (a) experimental set-up, (b) the impeller.

Illustration: The flow field of (a) water (b)PAAm solution and (c) laponite suspension



Main results

In this study, the PIV technique was used for the first time to investigate the flow fields in HSAD. Results showed that both 1.00% (wt) PAAm solution and 3.00% (wt) laponite suspension displayed comparable rheological signature of highly shear-thinning viscosity as for HSAD digestate. Moreover, the 3.00% (wt) laponite suspension was a colloid-liquid structural fluid, then very similar to the HSAD digestate that is a solid-liquid mixture. The order of mixing difficulty can be: 3.00% (wt) laponite suspension > 1.00% (wt) PAAm solution > water. Both the small flow velocity and the very located mixing zone around the impeller reveal that the efficient agitation of real HSAD digestate requires advanced mixing strategy with multilayer impellers arranged abreast for example. The high energy consumption of these complex media also imposes the development of new mixing techniques. Furthermore, the use of transparent model fluids such as laponite suspension in transparent pilots could contribute significantly to the improvement of existing techniques by better understanding the complex flow and mixing mechanisms.

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2017



Undressing a water marble on oil film

Xiaofeng JIANG (3rd year)

Huai-Zhi LI
Axe 1 | SysPol |



Keywords: Liquid marble, superhydrophobic, undress, oil film, particles

General context, scientific issues

In the early 20th century, stabilized interfaces by particles were conceptualized due to Pickering emulsions^[1]. Nowadays, particles can be manipulated to stabilize an individual drop which is firstly named as “liquid marble” by Aussillous and Quéré^[2]. Liquid marbles are non-stick water drops encapsulated with micro- or nano- metrically superhydrophobic particles. In the past decades, many interests were focused on liquid marbles due to their various applications such as micro-reactors, micro-pumps, gas sensor, blood typing, electrowetting, optical probing, cell culture, to name only a few^[3-5]. To our best knowledge, the dynamics of undressing hydrophobic particles around liquid marbles by an oil film has never been reported.

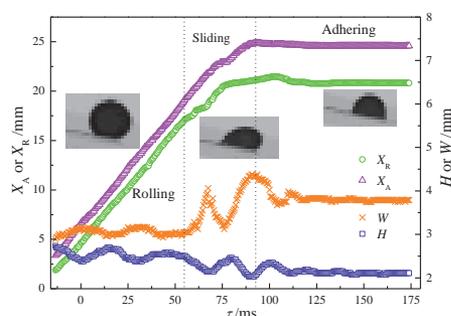
Objectives and stakes

This work aims at investigating how liquid marbles move on oil film and to what extent enveloping particles can be progressively undressed to immobilize finally the drop, expecting to facilitate the optical probing from the transparent bottom of liquid marbles.

Methodology / Experimental approach

Lycopodium particles are hydrophobic and the mean diameter of these particles is around 20 – 50 μm . Water drops of given volumes controlled by a precise microdosing syringe (range: 0 - 100 μL) are released to a bed of Lycopodium particles to form liquid marbles. In order to investigate the undressing dynamics of a liquid marble on an oil film, a rolling slope device was designed. Through a small spoon, the newly formed liquid marble could be transferred to a glass slide. The slope of the glass slide (total length is 6 cm) was set to be $\theta = 10^\circ$ and a thin layer of silicone oil was brushed gently with a tissue. Four silicone oils: SO 5, SO 10, SO 50 and SO 100, were applied to form the oil film. The motion velocities and deformation details can be quantitatively obtained from image analyses through a Matlab program.

Illustration: Dynamic undressing process



Main results

- There exist three distinct stages during the marble-capturing process: linear stage (rolling), transient stage (sliding) and attaching stage (adhering).
- A near constant rolling velocity is maintained until a physical contact between water and oil film when superhydrophobic particles begin to be removed at the base of the liquid marble.
- The contact angle of captured marbles after undressing is similar to that of static water drops on oil film, providing evidence that the bottom of liquid marbles is nearly void of particles to display a water-oil direct contact.
- The larger the liquid volume, the longer the distance for marbles to undergo; the larger the oil viscosity, the quicker the transient stage to immobilize liquid marbles.

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<p>2017</p> 	<p>Hydrodynamics in industrial plants cooling circuits: influence on fouling phenomena, characterisation and compartmental modelling</p> <p>Nicolas JOURDAN^{1,2} (1st year)</p> <p>Olivier POTIER¹, Thibaut NEVEUX², Mohamed KANNICHE²</p> <p>Axe 1 ¹SOLEO ²EDF</p>	
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Keywords: Hydrodynamics, Cooling circuits, Fouling phenomena, Compartmental modelling, Experimental characterisation

General context, scientific issues

The use of natural raw water in industrial cooling systems of electrical plants causes fouling phenomena that reduce heat transfer efficiency. Water heating and evaporation in the cooling cycle induces precipitation of calcium carbonate, particles deposition and biofilm development, hence the use of additives to inhibit these fouling phenomena. The control of these treatments requires a strong knowledge of physical and chemical phenomena in the system.

Objectives and stakes

The objectives of this study are to provide an accurate description of the hydrodynamic conditions in each circuit unit operation, and to model all the parameters influencing the fouling phenomena.

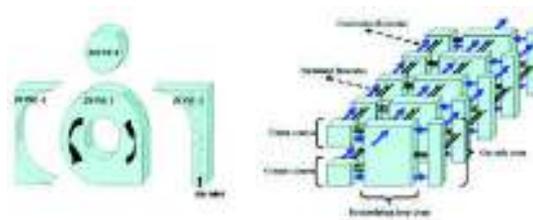
Methodology / Experimental approach

The methodology can be divided in three main steps. The first step is a characterisation of the hydrodynamics conditions in each part of the circuit. Experimental data on full-scale process being difficult to obtain, hydrodynamic conditions will be obtained using CFD simulations and experimental measurements on pilot scale reactors: transfer phenomena will be studied on EDF pilot plants and water flow of cooling towers packing will be observed on a specific pilot scale reactor.

The second step consists in the model construction. The choice of compartmental modelling will be justify by the bibliography study [1]. Each physical, chemical and biological phenomenon will be investigated independently in order to identify representative parameters. Then, a global scheme of phenomena interdependence will be built as a shape of the compartmental modelling organisation.

The third step will gather theoretical, simulated and experimental data to develop a global construction method for the compartment modelling of the cooling circuit. The modelling approach will be scaled up to a real size cooling circuit.

Illustration: Compartmental modelling construction; Example for wastewater treatment plant [1]



Main results

The main part of the performed work is a bibliography study, and the conception of the pilot scale reactor.

The main phenomena influencing fouling or hydrodynamic of the system were identified: transfer phenomena, precipitation of calcium carbonate, particle deposition, biofilms and different regimes of water flows (e.g. falling drops, water films, flow in condenser tubes, flow in the cool basin). Heat transfer phenomena are well known in cooling towers [2] but mass transfer coefficients need to be obtained with experimental setups. Also, calcium carbonate and biofilm growth are well-known in specific conditions. The study of hydrodynamic characteristics will determine in which model can be use and implemented in the compartmental modelling [3]. Finally, the flow conditions in each part of the circuit can be investigated: in the tower, falling drops and falling films on the packing were studied in general case to create the experimental pilot scale reactor [4, 5].

The pilot scale reactor will be a cuboid column of 20cm x 20cm with HD cameras. The conception started by sizing the water distribution system and the air injection system. The reactor is currently built at the LRGP Atelier.

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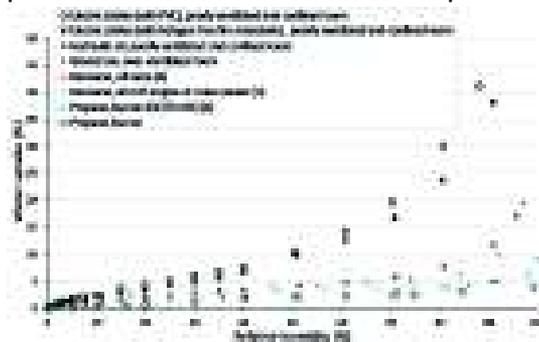
2017	Study of sorption mechanisms of water on aerosols issued from fire : identification of the influencing physico-chemical parameters	
	<u>Laura Lintis (2nd year)</u> F.X. Ouf ¹ , A. Coppalle ² , C. Vallières ³ [1] Institut de Radioprotection et de Sécurité Nucléaire [2] UMR 6614 CORIA, CNRS, Université et INSA de Rouen [3]LRGP AXE 1 SAFE	

Keywords: fire hazard, soot, water sorption, HEPA filter

General context, scientific issues

Fire is the most likely hazardous risk in a nuclear facility and can lead to emissions of radioactive particles and soot in the atmosphere. In case of fire, soot particles strongly interact with gas/vapours and may significantly modify the properties of the cake formed at the HEPA filter surface. Indeed some adsorbed species such as water on soot surface may be a significant parameter on the clogging process [1, 2]. Sorption phenomena on soot have to be taken more in account in order to improve the fire modelling, to better predict the clogging of the HEPA filter and prevent their damaging or breach in the worst case.

Illustration: Water sorption isotherms on soot particles emitted from different combustion process



Objectives and tasks

The principal aim of this study is to develop a model of water adsorption/condensation (AC) on soot emitted in fire conditions. This model would be developed by determining the most influencing physicochemical parameters of soot on the water sorption process.

Main results

The illustration represents several isotherms from literature [4] and from water sorption measurements on different soot produced during fire experiments. Fire soot seems to be more hygroscopic than those emitted by propane burner. The difference of water affinity between electrical cables soot (first one with PVC, the other one with HFFR) may be due to chemical composition. Hydrocarbon fuels produced from similar flame type (Kerosene in an oil lamp, hydraulic oil in a confined room) present similar water sorption. Further experiments with other fuels, burning conditions and scales will enable us to enlarge the data base of water sorption isotherms and physicochemical properties of soot. Thus empirical relationships between soot and fire parameters could be deduced. Finally the most influencing parameters of soot on their hygroscopicity could be determined in order to improve an adsorption-condensation model (AC) already proposed in the literature [3].

Methodology / Experimental approach

Experiments consist in producing soot from realistic fire conditions, analyzing their characteristics and determining their water sorption isotherms. First, soot of isolated fuels commonly used in nuclear facilities (Plexiglas, PVC) are produced and collected at bench scale in a controlled atmosphere calorimeter cone. Online analyses are performed in order to determine the mass, number and surface concentrations of the soot. Other soot from more complex elements (glove boxes, electrical cables) are collected during fire tests made at realistic scale. All those collected particles from different fuels are characterized for determining the morphology (fractal structure, overlap coefficient Cov), the particle size, the chemical composition, the specific surface area, the elemental to organic carbon ratio and the condensed material content TC. Finally water sorption measurements are carried out with microbalances at atmospheric pressure and under vacuum. These data bases of physicochemical properties and sorption isotherms will enable us to develop a water adsorption model suitable for realistic soot and including the most influencing parameters.

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<p>2017</p> 	<p>Study of the Gas-Liquid dispersion in static mixers</p> <p><u>Marco SCALA (1st year)</u> Huai-Zhi LI, Lionel GAMET Axe 1 SysPol </p>	
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Keywords: Static mixer, gas-liquid flow patterns, modeling, local measurements, numerical simulation

General context, scientific issues

Static mixers are often used in Industry for mixing miscible or partially miscible fluids, for the dispersion of immiscible phases, performing chemical reactions, etc. There are diverse static mixers with different geometries and sizes. Even though they are interesting tools for the intensification of mixing and reaction operations, only a few studies have been performed in order to characterize and understand the multiphase flows (G/L and L/L) at the millimetric scale in the laminar regime, at low flow rates of the dispersed phase.

Illustration: Experimental setup at LSGC



Objectives and stakes

The main objective of this PhD thesis is to characterize the G/L dispersion in different types of millimetric-sized static mixers and at different operational conditions (laminar regime at low flow rate of the dispersed phase). To characterize the fundamental local phenomena related the interactions between the different phases with the static mixer, optical methods will be used. In the first part of the PhD the student will develop a methodology to characterize the flows inside the static mixers in order to describe the mechanisms of bubble deformation, break-up and coalescence through the mixer. The developed methodology will be employed in the second part of the PhD thesis to characterize the flows at different operational conditions and define maps of flow regimes. The hydrodynamic study will be complemented with mass transfer rates and mixing time measurements. An experimental method to measure the G/L mass transfer rate and mixing time in the liquid phase inside static mixer will be also developed. In the third part of the PhD a CFD model will be developed.

Main results

- The experimental setup with suitable and variable transparent static mixers was realised.
- Preliminary experimental measurements of the flow fields were performed by the PIV technique in presence of gas bubbles.
- First tests were carried out for the mass transfer between bubbles and a liquid in presence or absence of surfactants.

Methodology / Experimental approach

- 3D printed transparent static mixers;
- Particle Image Velocimetry (PIV) in both aqueous (LRGP) and oil (IFP) phases;
- Mass transfer between gas bubbles and a liquid phase
- CFD modeling and simulation.

References

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2017



Alternative process for the cleaning of blast furnace fumes

Guillemette Thieffry (4th year)

Augustin Charvet, Nathalie Bardin Monnier, Dominique Thomas

Axe 1 | SAFE



Keywords: Aerosol, Dust separation, Filtration, Trickle bed

General context, scientific issues

Steel industry is known to be responsible for high emissions of CO₂ [1]. They can be reduced by lowering the carbon consumption or by upgrading or storing carbon dioxide emissions. The VALORCO project adheres to this objective and proposes both to reduce at source the quantity of CO₂ and to value those emitted. These last solutions require a gas free from particles or at least with a very low dust content.

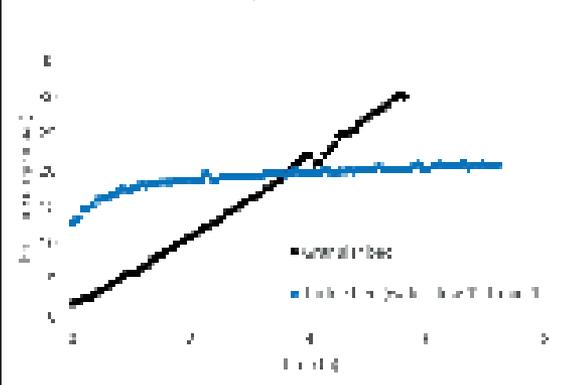
Objectives and stakes

Systems are already in place for the treatment of gases produced by the steel industry. However, if they aim at respecting air emission standards, the processes of CO₂ valorization require to introduce a new step in the treatment chain. With that objective in mind, we developed a trickle bed filter. It is comprised of a fixed bed of particles which is passed through by a liquid and a gas flow. In our dedusting application, the gas is filtered through a stack of collectors and the collected particles are continuously re-entrained thanks to a low water flow rate. The main difficulty in the design of a trickle bed is the selection of the operating parameters (air and liquid flow rates) and the bed characteristics (collector diameter) in order to obtain a good efficiency (as close as possible to a filter media efficiency) while maintaining a constant and limited pressure drop.

Methodology / Experimental approach

The experiments have been carried out in a co-current configuration on a 2.5 m-high glass column with a diameter of 0.2 m. The bed is 0.5 m high and different collectors have been used. An aerosol composed of Al₂O₃ micronic particles is generated and collected through the granular bed. Water is pumped from a tank and a distributor is used to wet the collectors homogeneously. A pressure transducer and an aerodynamic particle sizer allow us to determine the performances (pressure drop and collection efficiency) of the filter. As there is no correlation for determining the theoretical collection efficiency and pressure drop of a trickle bed, the performances of this separator have been compared with those of a traditional granular bed.

Illustration: Pressure drop in clogging experiment for a granular bed and a trickle bed (glass beads collectors with a diameter of 5 mm)



Main results

Hydrodynamic and initial efficiency measurements showed that the presence of water leads up to an increase in the pressure drop and the initial efficiency. The best configuration was for an air flow rate of 20 m³.h⁻¹, a liquid flow rate of 12 L.min⁻¹ and using collectors of 5 mm diameter. Clogging experiments validate our approach, revealing a good collection mass efficiency (89%), and a pressure drop that stabilizes during clogging and remains low in comparison to a dry granular bed (see the above illustration). The experiments showed a stable pressure drop during more than 30 hours, and as we used an aerosol with a concentration much higher than the particle concentration at the end of the actual treatment chain of the blast furnaces we can suppose that these trends can be extrapolated to much longer times.

The next step is now to model the pressure drop and the collection efficiency of the trickle bed in order to design an industrial pilot.

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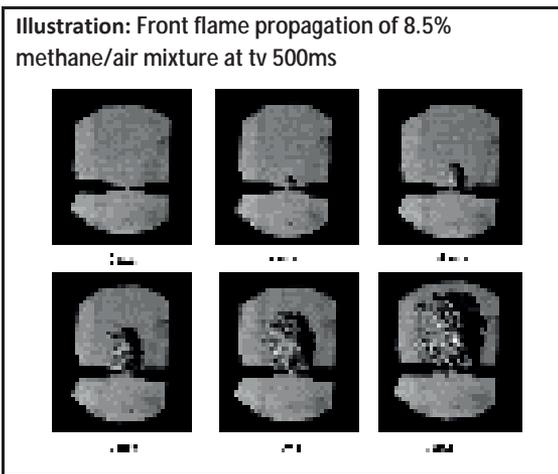
2017	Effects of Nanoparticles Insertion on Gas Mixtures Explosions <u>David TORRADO (3rd Year)</u> Olivier DUFAUD, Pierre-Alexandre GLAUDE Axe 1 SAFE	
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Keywords: Hybrid Explosions, nanoparticles, carbon black, flame velocity

General context, scientific issues
Hybrid mixtures explosions of flammable gases and combustible powders, each of which could be in amount less than the lower respective explosible limit/concentration, are often present in industrial processes (mainly coal mines and power generation plants). Recent studies of the explosible characteristics of these systems have been conducted. However, there is a limited information regarding the combustible nanopowders/gases mixtures. This project focuses in carbon black nanopowders/gases mixtures because they may also allow to understand the influence of soot in the combustion phenomena

Objectives and stakes
The objective of this thesis project is to determine the influence of nanoparticles insertion (mainly carbon black) on gas mixtures explosions. The effect of soot or soot's precursors in the combustion of gases will be also studied

Methodology / Experimental approach
The explosion severity of nanopowders/gas mixtures has been studied by measuring the maximum overpressure, the rate of pressure rise and the front flame velocity. A 20 liters explosion sphere is used in order to determine the evolution of the two first parameters as a function of the nanoparticles concentration, the gas molar fraction and the initial system turbulence. The combustion gases are analyzed by micro-chromatography. The flame velocity is measured by the open-tube method. Dust clouds are generated by an air pulse from the bottom of the tube. A high speed video camera is used for recording videos of the flame propagation. The laminar flame velocity is approximate by taking the flame stretching into account.
For the flame detection, an optical set-up have been implemented in order to obtain Schlieren images. This technique is based on the detection of the changes on the refractive index (which depends on the temperature and concentration of the mixture).



Main results
The maximum overpressure and the rate of pressure rise has been measured for nanocarbon-black/methane/air and were compared to the reference system methane/air mixtures. The severity tests had been held for two types of carbon black with similar size distribution, but different size of elementary particles. The results shows that the insertion of carbon blacks at low concentrations does not modify significantly the maximum overpressure, whatever the initial turbulence and gas concentration. However, the rate of pressure rise slightly decreases when carbon black is added, especially at high turbulence and methane-rich mixture. At high turbulence, the influence of carbon black insertion on the explosion severity is less perceptible for particles with higher primary diameter. The flame velocity seems to decrease when carbon black nanoparticles concentration is increased. These trends are explained due to the improvement in radiation heat transfer with the addition of black particles.

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2017



CO₂ sequestration by mineral carbonation in steel production Treatment of solid particles for recovery of valuable metals

Laura TURRI (4th year)

François Lapicque, Hervé Muhr

Axe 1 | SYSPOL



General context, scientific issues

Valorco is a project coordinated by ArcelorMittal, in order to develop steel industry with low carbon dioxide emissions. The global project consists of a sequestration process by mineral carbonation, an alternative in which CO₂ is captured and chemically stored in solid carbonates. Olivine has been selected as mineral feedstock: it is a magnesium-iron silicate (Mg,Fe)₂SiO₄ that also contains small amounts of other metals. In particular, chromium oxide, inert during the carbonation, is present in the chromite particles (Cr₂O₃-FeO) at a concentration of 0.20-0.25 wt %.

Objectives and stakes

To ensure environmentally responsible process, separation technologies are studied for the recovery of valuable compounds and to avoid disposal of toxic solids. A part of the study is focused on olivine treatment before carbonation to collect the chromite particles by flotation.

Methodology/ Experimental approach

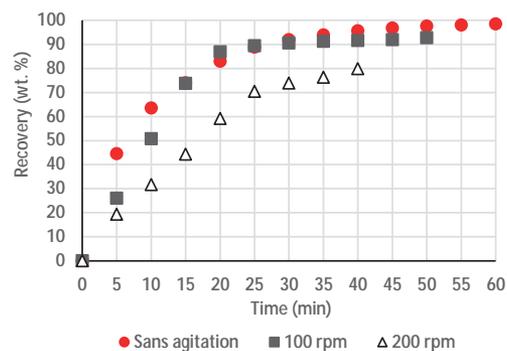
The flotation system developed in the lab consists of a column whose plug includes the SS sparger distributor with "05" porosity for homogenous gas distribution and an appropriate bubbles size. For circulation of the slurry, a second system has been developed with a mechanical agitation, considering the magnetic properties of chromite particles. The tests have been conducted in a solution of CTMAB as collector (150 mg/L) at pH = 11, using a mixture of olivine and 3 wt % of additional chromite to enhance the results interpretation and to control the chromite characteristics. The selectivity and the recovery extent of the collected particles are analysed to determine the optimal test conditions. A numerical law which corresponds to a calibration relationship is established between the chromium relative concentration, obtained by EDX analysis, and the chromite particles fraction in the solid. The model consists of a second order polynomial function, based on the experimental results.

Illustration

Recovery of chromite particles by flotation obtained for various stirring rate.

$$\text{Selectivity} = \frac{\text{Chromite concentration}}{\text{Input chromite concentration}}$$

$$\text{Recovery} = \frac{\sum_{i=0}^i \text{Chromite particles collected by flotation}}{\text{Total of chromite particles}}$$

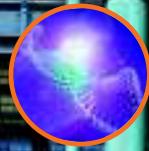


Main results

According to the tests results and considering hydrodynamic aspects, agitation influences the gas introduction and the bubbles dispersion in the column. Experiments reveal that the increase in the agitation rate affects the dispersion of the gas in the column, up to a certain liquid level from the bottom. Best selectivity and recovery are obtained for the tests without agitation. After 5 min flotation, the mass of the collected particles is near 5 %. A concentration of chromite particles is observed with a selectivity of 9 and a recovery of 45 %. After 15 min, the selectivity decreases and 25-30 % of the particles are collected with a chromite recovery of 80 %. From 15 min to 60 min, which corresponds to the end of the test, the selectivity is lower than 1; from that time, flotation is not selective and does not allow the chromite concentration in comparison to the input chromite fraction. Flotation cycles with the reuse of collected particles are considered to increase the selectivity.

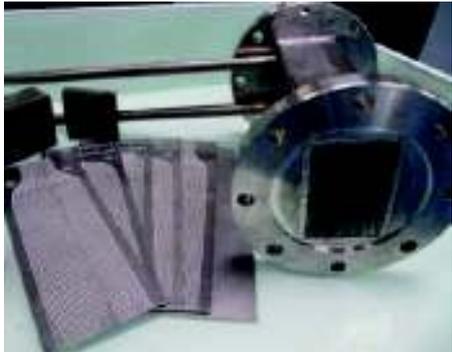
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PRIMO

PROCESSES, REACTORS, INTENSIFICATION,
MEMBRANES, OPTIMIZATION

<p>2017</p>  	<p align="center">Compact heat exchanger reactor modelling</p> <p align="center"><u>Jean-Patrick Barbé (3rd year)</u></p> <p align="center">Laurent Falk, Jean-Marc Commenge</p> <p align="center">Axe 2 PRISM Air Liquide Centre de Recherche Paris-Saclay</p>	
<p>Keywords: Heat exchanger-reactor, plate-fin heat exchanger, process simulation, reaction, catalyst, reactive fin efficiencies, microchannel.</p>		
<p>General context, scientific issues</p> <p>In the specific case of hydrogen production by Steam Methane Reforming (SMR), high power heat exchangers (hundreds of MW) are operated to conduct the endothermic catalytic SMR reaction. The operating conditions are harsh: high temperatures, high pressures, highly corrosive environments and poor heat transfer, leading to low process efficiency [1].</p> <p>Process intensification by miniaturising the heat exchanger reactors allows reducing the limiting phenomena (internal and external mass transfer, heat transfer, ...) inherent to catalytic reactions [2][3]. However, the lack of proper sizing tools makes the implementation in a global flow sheet and the economic assessment of such technologies difficult.</p>	<p>Illustration: Milli-structured, plate and channel - heat exchanger reactor, with examples of the plates.</p> 	
<p>Objectives and stakes</p> <p>The objective of this project is to develop a simulation tool for heat exchanger reactors, which is able to simulate endothermic and exothermic catalytic reactions and predict thermal profiles and efficiencies. A simplified 1D version of the tool will be developed and validated with experimental and CFD simulation results. The CFD simulation should also allow understanding the physical phenomena occurring in the heat exchanger reactor.</p>	<p>Main results</p> <p>Several heat transfer phenomena occur in plates and fins heat exchangers, such as convection and conduction. The competition between both is responsible for non-negligible temperature gradients in fins [4]. In the specific case of reactive plates and fins heat exchangers, by absorbing or releasing heat at the fin surface, the catalytic reaction affects significantly the fin and by-pass efficiencies. As a consequence, the classical expressions available in the literature for these efficiencies are no longer correct. Not taking into account these differences would lead to overestimating both heat transfer and kinetics, the last one being critical because the kinetics depend exponentially on the temperature.</p> <p>A new simplified fin model was developed at channel scale in order to estimate heat transfer, reaction and by-pass efficiencies for a reactive fin. Even if restrictive assumptions had to be made, this model shows very good agreement with a real fin subjected to a real flow simulated in Fluent.</p> <p>At exchanger scale, the competition between conduction, convection and heat absorption was investigated and showed very little impact on the Air Liquide heat exchanger reactor performances.</p>	
<p>Methodology / Experimental approach</p> <p>The 1D program which is currently under development includes homogeneous and heterogeneous models (featuring external heat and mass transfer considerations) that enable the simulation of simultaneous catalytic and fluid phase chemical reaction in a heat exchanger. Plate-fin heat exchanger was chosen as general frame for the simulation tool.</p> <p>The CFD simulation of both a reactive flow in a channel and a set of several channels are done to understand the physical phenomena occurring at local and global scales respectively (i.e. external and internal mass transfer, coupling between heat and mass transfer, conduction, non-uniform distribution in the channels, ...). These simulations investigate the impact of major assumptions that were made to simplify the model, such as heat conduction effects in a section of the metal frame, perpendicular to the flow.</p>	<p>References</p> <p>[1] L. Prost, Air Liquide S.A., 2014, ENSIC conference [2] Xu et al., AIChE Journal, 1989, Vol. 35, n°1, p 97-103 [3] Commenge et al., CR. R. Physique 5, 2004, p 597-608 [4] Shah et al., Compact heat exchangers, Hemisphere Publishing, New York, 1990, p 727 - 742</p>	

2017	Dynamic real-time optimization of a graft polymerization process <u>Bousbia Salah Ryad (3rd year)</u> Supervisors: Abderrazak Latifi and François Lesage Axe 2 ODCa	
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Keywords: Graft polymerization process, dynamic optimization, moving horizon state observer, experimental implementation.

General context, scientific issues

Real-time optimization (RTO) has emerged as an essential technology for optimal process operation in the chemical industry. It is a closed-loop optimizer based on a steady-state model. The most common RTO method used in industrial applications is the two-step approach. It consists of solving two optimization problems: the first one is a parameter estimation to update the model, and the second one is the resolution of an optimization problem to minimize the cost function, using the updated model to find new improved operating points [1]. Thus, as the number of iterations increases, the model becomes more accurate.

Another interesting RTO method is the modifier adaptation approach that modifies, at each iteration, the optimization problem in order to match the real-plant to the Karush–Kuhn–Tucker (KKT) point, upon convergence [2].

It is noteworthy that RTO has demonstrated its performance in many industrial applications, but has also shown its limitations for processes with frequent transitions and long transient dynamics. Recent advances have transformed the steady-state RTO to dynamic real-time optimization (D-RTO) based on a dynamic process model, hence allowing the performance indices evaluation with higher frequency. Furthermore, D-RTO makes use of the online available measurements to maximize a process performance index while meeting environmental and operating constraints. On the other hand one of the most interesting features of D-RTO is it uses a more general cost function that represents the process economics rather than the tracking error [3].

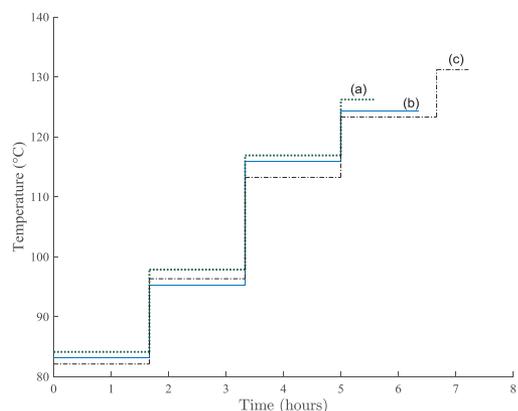
Objectives and stakes

The objective of the present work is to develop and apply a D-RTO methodology to a graft polymerization batch reactor. The goal is to minimize the batch period subjected to some terminal industrial specifications (i.e. conversion rate and grafting efficiency) with the reactor temperature and batch period as decision variables.

Methodology / Experimental approach

The D-RTO approach developed consists in coupling an on-line dynamic optimization method with a moving horizon estimator (MHE) in a closed loop control. The resulting optimal profiles will be implemented within a batch polymerization process [4].

Illustration: Optimal profiles of the reactor temperature with different final constraints.



The Process is a batch reactor where polymer grafting reactions take place. The objective is to value the used ground tire rubber. The latter results from the grinding of the rubber part of used tires which retains excellent elasticity. The idea is to take advantage of its elasticity to toughen brittle polymers such as polystyrene upon incorporating GTR into them. The kinetic scheme and reaction rates as well as reactor design equations are detailed in [4].

Main results

The illustration above presents the optimal-time profiles of the reactor temperature obtained for a grafting efficiency of 75% and for three different values of the final conversion rate: (a) 85%, (b) 90% and (c) 95%. They exhibit a regular increase in order to fulfill the required monomer conversion rate and grafting efficiency. This regular increase is meaningful since at constant temperature, the conversion rate increases with time whereas the grafting efficiency decreases. Therefore the temperature should increase with time in order to achieve the desired conversion rate but not too much in order to guarantee the specified terminal value of grafting efficiency.

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<p>2017</p> 	<p>PhD subject : Optimization of Architecture of Membrane Process</p> <p><u>Marjan Bozorg (1st year)</u></p> <p>Supervisor 1 Christophe Castel, Supervisor 2 Bernardette Addis, supervisor 3 Veronica Piccialli</p> <p>Axe 2 EMSP LORIA</p>	
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Keywords: Multicomponent gas mixture, Separation process, Membrane network, Global optimization, Mixed integer nonlinear programming

General context, scientific issues

Among the numerous applications of the membrane separation processes in industry, gas permeation is a very promising separation technology. To optimize the performances and the global costs of such processes, the development of accurate and reliable design strategy is essential. This strategy requires rigorous mathematical modeling approach in order to optimize the process architecture and the operating conditions of membrane separation systems for the separation of multicomponent gas mixtures.

Objectives and stakes

The objective of this thesis is to develop a methodology which aim is to design the optimal structure of membrane systems in order to simultaneously minimize operating and/or capital costs while guaranteeing separation performances of the system.

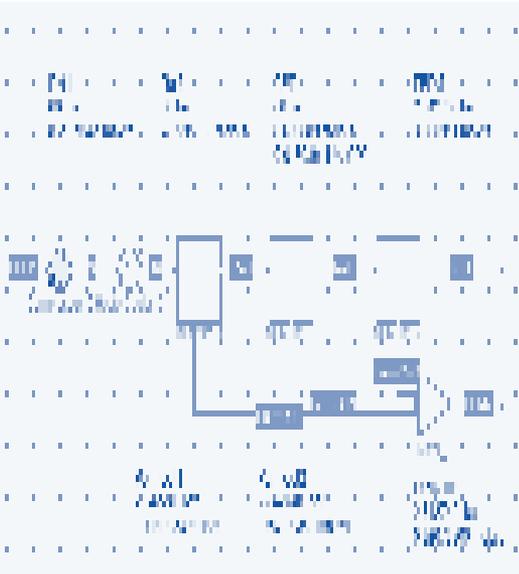
Methodology / Experimental approach

The problem of the optimization of Separation of multicomponent gas mixture membrane system is classified as a non-convex Mixed Integer Nonlinear Programming (MINLP) problem. Therefore, a specialized version of Monotonic Basin Hopping (MBH) as the basis of many elaborate Global Optimization (GO) heuristics was proposed in this study that exploits the structure of the problem.

The first step of this study was to compare, on a real case study, the separation of acid gases from crude natural gas, published optimized architecture (Runhong Qi, 2000) with the resulting architectures of our optimization method. Based on the simultaneous minimization of the operating expenses and capital investment of the system and maximization of the CO2 recovery and considering the same objectives, constraints and economic model, the MBH algorithm has been adapted to the specific application. A Mathematical Programming Language (AMPL) has been used to implement the proposed MBH optimization model. A final validation of the results by

a dedicated membrane simulation tool (MEMSIC) used in a classical PSE environment ensures the practical interest of the configurations confirming the effectiveness of the proposed method.

Illustration: Optimal 3-stages membrane network



Main results

Regarding the global cost of the separation process, a considerable improvement of the membrane process configurations published by (Runhong Qi, 2000) has been found. A new multistage membrane system architecture has been proposed, which is different both in terms of the involved membrane areas, pressure and distributed flows.

References

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<p>2017</p> 	<p>PhD subject: Study of uranium dioxide in nitric medium. Toward a model for dissolvers.</p> <p><u>Florence Charlier (3rd year)</u></p> <p>Eric SCHAER, Alastair MAGNALDO Axe 2 PRISM CEA MARCOULE</p>	
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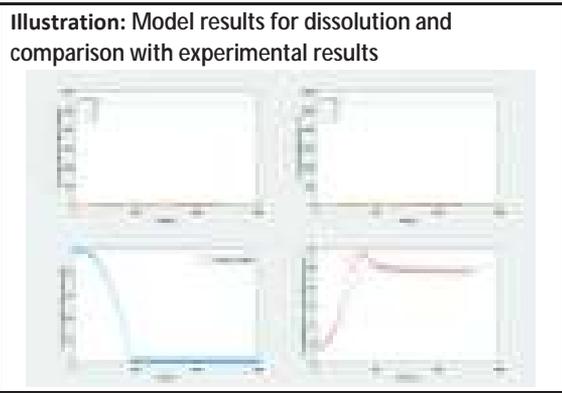
Keywords: Autocatalysis, mass transfer, solid-liquid-gas reaction, hydrometallurgy, kinetics, model.

General context, scientific issues

In France, Nuclear fuel recycling relies on liquid – liquid extraction of uranium. Dissolution is hence a milestone at the head end of the recycling process as it enables to put the radionuclides in solution. This step hence designs the entire industrial plant. This study is about uranium dioxide as nuclear fuel still contains 96% of this element after it has been used for electricity production in nuclear reactors.

Objectives and stakes

UO₂ dissolution in nitric medium is a complex reaction. First of all, the dissolution produces nitrous oxide. Three different phases must then be considered, including the mass transfer problematic linked to them. Secondly, one of the reaction products accelerates the reaction kinetic; the dissolution is then called autocatalytic [1]. The kinetic for this kind of reaction needs to be formalized in order to be included in a global model for dissolvers. This model will then be used to optimize the dissolution process.



Methodology / Experimental approach

Kinetic study: Dissolution rates were measured by optical microscopy. Perimeter and surfaces are determined by image treatment realized on Matlab. The disappearing volume leads to a dissolution rate in nm/s. The advantages of this method are a better control of mass transfer and catalyst accumulation. Moreover, it is more precise than following species in solution and it is in situ. Finally there no preparation needing and few effluents are produced.

Solutions were filled with catalyst and it was shown that they tended to lose reactivity during time. The influence of degassing was hence suspected. It was studied by varying the liquid gas exchange in the solution. Reactivity was also tested while introducing nitrous oxide in the solution.

These observations were included in a model considering gas-liquid exchange and a reaction between catalyst and nitrous oxide. The influence of temperature and NO_x partial pressure was tested thanks to this model.

Experiments were also realized at a macroscopic scale to verify the phenomenon discovered thanks to microscopy.

Main results

The global kinetic was defined by a two-step mechanism: a non-catalyzed reaction leading to catalyst production and the catalyzed reaction. The kinetic orders for the catalyst and nitric acid, as well as the activation energies were defined for both reactions.

It was demonstrated, for the first time, that the catalyst is linked with nitrous oxide. This explains the loss of reactivity observed for high temperature in literature [2].

A computational model, taking into account species diffusion and the reaction particularities, was elaborated to study more precisely the phenomenon. It describes well the sigmoid aspect of the dissolution curve obtained by microscopy.

New areas of evolution for dissolvers were determined thanks to this model. Temperature and catalyst concentration can be optimized in order to reduce residence time in dissolvers. Moreover, NO_x were shown to be a lever to influence the reactivity in reactors.

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<p>2017</p> 	<p align="center">Intensification of a catalytic reactor for the production of acrolein</p> <p align="center"><u>Mathieu Chateau (2nd year)</u> Eric Schaer, Jean-François Portha Axe 2 PRISM Adisseo</p>	
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Keywords: Heat exchanger-reactor, kinetic modelling, process simulation, catalyst, CFD

General context, scientific issues
Acrolein is produced by the controlled oxidation of propylene. This reaction, carried out in a fixed-bed reactor with a supported catalyst, is a highly exothermic process and molten salt has to be used in order to efficiently cool down the reactor. Furthermore, an elevation of temperature can lead to secondary reactions, degrading the acrolein or competing with the main reaction.

Process intensification is an effective solution to these issues. Indeed, compact reactors have a high heat transfer coefficient, allowing a better temperature regulation and a better control of the process. [1]

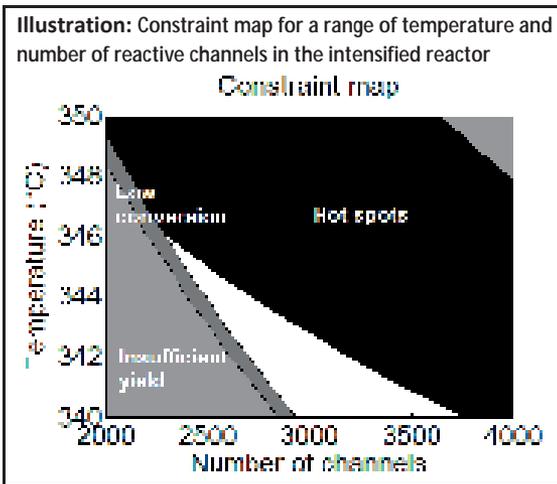
Objectives and stakes
The objective of this research project is to design, develop and operate an intensified heat exchanger reactor for the synthesis of acrolein by oxidation of propylene. This technology allows a good control of heat transfer and should limit unwanted secondary reactions.

Methodology / Experimental approach
In order to design a new reactor, the kinetics of the several reactions occurring in the reactor have to be clearly determined. A kinetic model, based on Redlingshofer et al. work [2], has been developed, with numerous kinetics parameters that have been estimated using experimental data provided by a team of the UCCS.

This new kinetic model was then used to design an intensified heat exchanger reactor, using a constraint map methodology.[3]

This design strategy consists in drawing a series of maps, presenting the performance of simulated reactors with various design parameters (channel width, length, and temperature).

In these maps, areas with sufficient performances can be determined, and gathering all of these maps lead to an acceptable area that complies with all of the constraints, and corresponding to the optimal design for the intensified reactor.



Main results
A preliminary design of the intensified reactor has been determined, and has been validated by a CFD simulation (ANSYS Fluent).

The preliminary design will be completed with a study of the distribution and collecting chambers.

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2017



Preparation and characterization of new polymeric membranes to improve drinking water facilities by membrane distillation

Tarik ELJADDI (PosDoc)
Supervisor: Denis ROIZARD
Axe 2 | EMSP



Keywords Membrane distillation, polymeric membrane, separation and purification, flux, desalination...

General context, scientific issues

The global capacity of seawater desalination plants is increasing by about 10% every year. Membrane technology has become a major technology to provide access to drinking water either by nanofiltration (NF) or reverse osmosis (RO).

On the basis of lab-scale and since recently semi-industrial scale experiments, membrane distillation (MD) has been demonstrated as an interesting alternative for brackish or seawater desalination. MD is a process involving the evaporation of water through the pores of a hydrophobic macroporous membrane. The liquid/vapour interface is supposed to be located at the membrane pore inlet. The membrane acts merely as a physical barrier between the two phases and has no influence on the process selectivity, but as it enhances the contact area for vaporization, this process is called a membrane contactor and is considered as a way for process intensification. The major potential risk of dysfunction of this process is membrane pore wetting, which is a key problem for membrane manufacturers and water companies that need some scientific-based guidelines before deciding to develop MD equipment. The project has a fundamental target, how to avoid wetting of porous hydrophobic membranes used in membrane distillation, in order to allow the development of new membranes to be applied for water desalting.

Experimental strategy

As explained above there is also a need of new membranes specifically dedicated to be used in the MD process, and which would have been designed specifically with the objective of reducing or to completely avoiding the risk of wetting. Indeed a drastic decrease of the membrane mass transfer coefficient would occur as soon as wetting takes place, due to the much lower diffusion coefficient in liquids (typically $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$) compared to gases or vapours (typically $10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$). In that event, a one to two orders of magnitude of the membrane mass transfer coefficient results, even for a limited wetting of the membrane such as 10% of the overall thickness of the porous media. In that case, the membrane becomes the major mass transfer resistance and the potentialities of the process, in terms of intensification and operational stability, no longer apply. It is thus of utmost importance to ensure non wetting conditions of the membrane; this objective has been intensively investigated for decades and it can be basically achieved through two main complementary strategies:

Develop non wetting porous membrane materials. In order to decrease and prevent membrane wetting, specifications of the MD membranes should be: a high surface hydrophobicity and roughness, a high porosity and pore size as large as possible, which is unfavorable to wetting, in order to reduce membrane resistance and to increase permeate flux. Today membranes used or studied for MD process are generally microfiltration membranes made of hydrophobic material like PVDF or PTFE but they were not specifically designed for MD operation.

There is thus another important challenge for the preparation of specific macroporous membranes for MD in order to combine both a high porosity and large pore size with a high hydrophobic and rough membrane surface.

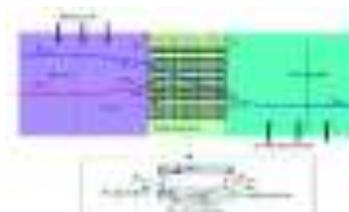


Figure 1 : Schema of heat and mass transfer through a single layer hydrophobic membrane used in DCMD process



Figure 2 : experimental setup (LRGP)

A complementary strategy consists to develop new membranes based on the above porous and hydrophobic membrane that will be further modified by surface treatment in order to tune the pore size and the surface hydrophobicity, in order to avoid any wetting. Providing that the chemical and physical modifications polymer are carefully chosen and correctly achieved at the porous surface, the resistance to wetting should be obtained without a too large decrease of the overall mass transfer coefficient. This concept is currently studied in LRGP for various membrane processes, but, to our knowledge, it remains unexplored for transmembrane distillation applications.

The novelty of this work and its originality are lying on: The general understanding of MD dysfunction and the search for advanced materials and tools to avoid wetting;

An experimental strategy that is planned in the same time to explore the ways of producing less wettable porous membranes by two complementary methods.

The effective membrane performance will be tested first at lab scale with plan membranes for water vapour mass transfer.

Acknowledgments:

The authors would like to thank ANR agency for Funding the Wetmem project.

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2017 	Conceptual design for CO₂ capture using membranes Giordano, Lorena (Post-doc) Supervisor: Denis Roizard Membranes, Séparations, Procédés Axe 2 EMSP	
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Keywords: carbon capture and storage, post-combustion CO₂ capture, mixed matrix membranes, MOFs, economic analysis, life cycle analysis.

General context, scientific issues

Mixed matrix membranes based on MOFs (M4) [1] are regarded as a promising technology to achieve a highly efficient CO₂ capture, due to their superior separation performances compared to conventional glassy polymers. Membrane-based CO₂ capture is also affected by the composition of the gas to be treated, as well as by the driving force for CO₂ separation [2]. Hence, the design of membrane processes based on M4 needs to be deeply investigated, in order to understand their technical behavior and to assess their potential benefits compared to well-established CO₂ capture technologies.

Illustration: Layout of a single-stage membrane system



Objectives and stakes

- Conceptual design of membrane systems for post-combustion CO₂ capture;
- Energy and economic analysis of single and dual-stage membrane systems for post-combustion capture at thermal power plants;
- Life cycle impact assessment of membrane separation processes.

Main results

Considering as a case study the exhaust flue gas from a coal-fired power plant, single and dual-stage membrane systems have been investigated and compared from the energy and economic points of view. The simulation study assessed the effect of varying membrane type (from the state of the art to newly design generation membranes), operating conditions and system layout on separation (CO₂ permeate purity and membrane area) and energy performances (net system power consumption and energy requirement per tonne of CO₂ separated). Additionally, the effects of membrane system integration within the power plant has been assessed by evaluating the plant capacity derating, the penalty on net efficiency and benefits on specific CO₂ emissions. Conversely, the economic analysis evaluated the specific cost of CO₂ capture and the mitigation cost with or without credits for enhanced oil recovery (EOR). Life cycle analysis of dual stage membrane separation processes has been performed varying the polymer type and the thickness of dense active layer; then a comparison has been made with CO₂ capture based on monoethanoalmine (MEA) absorption.

Methodology / Experimental approach

Membrane-based gas separation is simulated using the proprietary computer tool MEMSIC, considering a five-component gas mixture. The program is properly integrated into Aspen Plus V8.4 to perform the energy analysis of membrane separation system as a whole. Based on the costing methodology developed by the Electrical Research Power Institute, capital and operating expenses of membrane system are assessed. Then, the specific cost of CO₂ capture process is evaluated as the increase of electricity production cost of power plant per tonne of CO₂ captured in a year [3]. Life cycle analysis (LCA) of membrane systems is carried out using a hybrid approach, combining physical and economic input data. In this regards, environmental impacts of CO₂ capture process operation are evaluated through a conventional LCA, involving an inventory of materials and energy used during CO₂ separation and compression processes. Concerning the manufacturing and decommissioning, an economic input-output LCA is performed, based on cost data for producing and dismantling the capture system equipment.

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<p>2017</p> 	<p>PhD subject : Experimental characterization and design of a millichannel vaporiser</p> <p><u>Guillaume Henry (1st year)</u></p> <p>COMMENGE JM., PERE-GIGANTE A.</p> <p>Axe 2 PRIMO Thématique "Intensification"</p>	
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Keywords: Milli-channel, Vaporiser, Sizing, Design, Experimental study

General context, scientific issues
 Hydrogen is probably the fuel of the future. There is an ever-growing interest on its production and its new applications. Some of these require an on-site production; the storage of H₂ is a well-known issue. One of the goals of the FAIR project is to design an intensified SMR (Steam methane reformer). Two elements of the SMR are intensified: the heat-exchanger reactor and the vaporiser. The vaporiser will be designed to valorise waste heat provided by hot fumes leaving the heat-exchanger reactor.

Objectives and stakes
 The objective of this project is to design a milli-channel vaporiser providing the high-pressure steam required by the chemical reaction. Two different vaporisers will be designed: the first one will enable to understand hydrodynamics and heat-exchange that govern boiling in milli-channels at "low pressures" (1-5 bars); the second one will be the characterisation of a pilot-scale vaporiser made by additive manufacturing supporting "high pressures" (16-25 bars).

Methodology / Experimental approach
 The low-pressure vaporiser (LPV) is designed to operate under similar operating conditions than the high-pressure vaporiser (HPV). In a first step, the capacity of vaporisation in the HPV is estimated by the analysis of thermal resistances of the hot gas and the boiling water. In a second step, the LPV was sized using thermal oil as hot fluid. The hot side of the heat-exchanger was designed to meet the expectation of vaporisation. The sizing takes into account a maximal oil temperature of 220°C, corresponding to the flash point. The LPV is finally drawn thanks to Computer-Aided Drawing software.

Illustration: Structure of the LPV



From the left to the right: lid, window of visualisation, milli-structured plate, multitask block (distribution and collection of water, heating by oil convection)

Main results
 The vaporisation of water requires a lot of energy and it is a real issue to provide such a quantity. The geometrical configuration of the plate heat-exchanger reduces dramatically the exchange surface between the hot and cold sides. Therefore, according to the correlation of Nusselt number, the thermal oil presents higher thermal resistances than the boiling water. To achieve the heat transfer between oil and water, a forced convection is needed. The final version of the module is presented above, the dimensions of the section of the oil channel (first plate from the right) are 2.5 mm x 9 mm for a length of 1 meter. For a flowrate of 7 L/min, the average temperature of the oil is equal to 180°C.

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2017 	Experimental and numerical strategy for computer-aided identification of optimal intensified reactors <u>Zhengkun JIANG (Second year of PhD)</u> Jean-Marc COMMENGE, Jean-François PORTHA Axe 2 PRIMO	
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Keywords: Process intensification, Process modeling, Software development, Valorization of vegetable oil, Transesterification of vegetable oil by homogeneous base catalyst, Epoxidation of vegetable oil by percarboxylic acid

General context, scientific issues
 Since a few years, intensified reactors, such as plug-flow microreactors, are alternatives to stirred tank reactors. Thanks to their high heat and mass-transfer rates, a better control of operating conditions makes it possible to obtain a better product quality. However, it is difficult to predict quantitatively the real interest of intensified reactors without a large amount of experimental work. Hence, an iterative strategy [1] based on the combination of experimental design and modeling has been successfully developed to select the best reactor technology and corresponding optimal operating conditions while minimizing experimentation step.

Objectives
 The objective of this work is to develop a process intensification methodology and the corresponding software tool in which the users could optimize their experimental strategy in order to select the best reactor technology and corresponding optimal operating conditions.

Methodology / Experimental approach
 The process intensification software consisting of four functions (process modeling, parameter estimation, process optimization, design of experiments) is developed using MATLAB. The available types of reactors are continuous and fed-batch stirred tank reactors, microreactors and conventional plug-flow reactors. The systematic modeling method [2] is used for process modeling. While optimizing the performance and designing the experiments, multi-objective optimization algorithms, such as, genetic algorithm, particle swarm optimization, are included. The acceptance tests of the software are carried out thanks to two reactions concerned with valorization of vegetable oil:

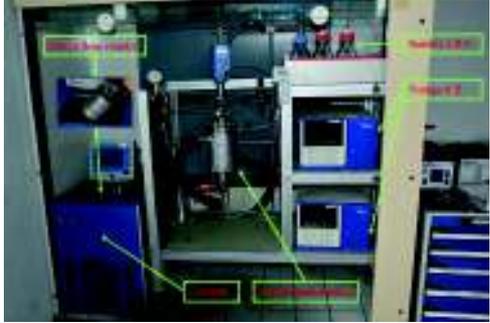
- transesterification of vegetable oil by homogeneous base catalyst.
- epoxidation of vegetable oil by percarboxylic acid.

Illustration:

Software running structure



Experimental device



Main results
 A literature survey providing theoretical basis has been carried out for the following aspects:

- process intensification strategy,
- systematic modeling methods,
- parameter estimation methods,
- multi-objective optimization algorithms,
- transesterification of vegetable oil by homogeneous base catalyst,
- epoxidation of vegetable oil by percarboxylic acid.

The process intensification software has been successfully developed. Current works aim at verifying experimentally the efficiency of the process intensification strategy and its range of validity.

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<p>2017</p> 	<p>New geometries for the improvement of mass transfer in membrane contactors applied to CO₂ capture and water desalination.</p> <p><u>Mejia Deisy (2nd year)</u></p> <p>Eric Favre, Cecile Lemaitre, Christophe Castel Axe 2 EMSP</p>	
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Keywords: Membrane contactors, Absorption, Intensification, Dean vortices

General context, scientific issues
 Dean vortices form when a fluid flows in a curved pipe. The centrifugal forces act on the fluid and the difference in velocity in the cross-section of the tube causes an imbalance of forces which leads to the formation of vortices called Dean Vortices. This phenomenon is widely used in various industrial applications to make them more efficient. The presence of secondary flows favors mixing, exchange rates, and transfer of material, heat, momentum and intensifies the mixture. (1)

Objectives and stakes
 There is still some negative points about membrane technology that have to be overcome in order to increase its performance and enlarge its field of application, therefore the main objectives of the project are:

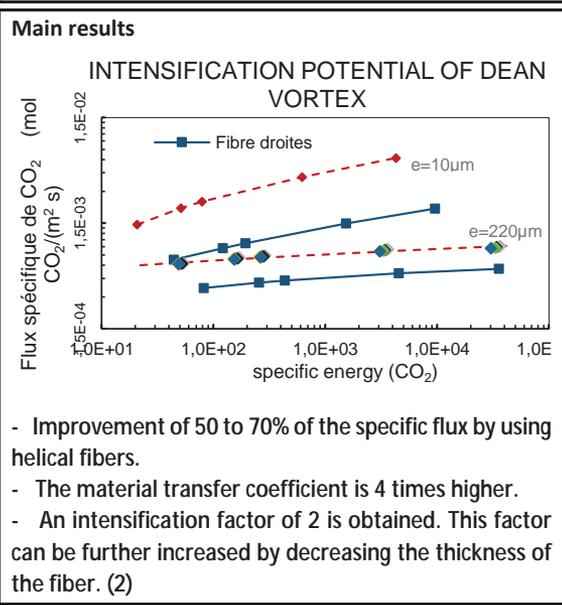
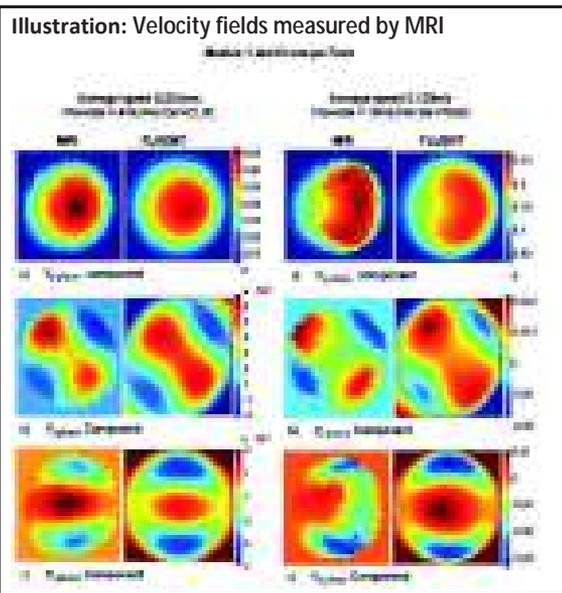
- CFD study of the Dean vortices
- Limitation of the concentration polarization in HF contactors by the implementation of the Dean vortices
- Find the best geometry parameters to maximize the energetic performance and flux of the contactors.

Methodology / Experimental approach
 A computational fluids dynamics tool is used to simulate the mass transfer through a dense membrane.

First, classical geometry (straight fibers) was simulated in order to validate the mass transfer and hydrodynamics with experimental data. Then, simulations of the helical geometries were done to find the configuration of parameters that give the best flux and energetic performance.

The transferred flux was also measured experimentally and the vortex were observed using magnetic resonance imaging (MRI).

The same procedure is applied for the CO₂ absorption in water and for water desalination, in this last application both the heat and mass transfer are improved thanks to the vortex presence.



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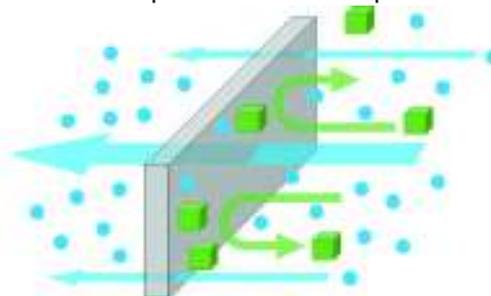
<p>2017</p> 	<p align="center">Study and development of hybrid processes integrating membrane technologies for purification of bio-based molecules</p> <p align="center"><u>PICAUD VANNEREUX Simon (2st year)</u></p> <p align="center">Denis ROIZARD, Eric FAVRE Axe 2 EMSP EURODIA INDUSTRIE</p>	
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Keywords: Pervaporation, vapor permeation, membrane contactor, hybrid processes, sustainable development, bio-based molecules, purification processes, energy efficiency, simulation, modelling

General context, scientific issues

In the current context of sustainable development at all society levels, the industrial demand concerning bio-based products grows very strongly. However main actual separation processes are focused on products from fossil resources and are not already suitable with bio-based products. This situation acts as a brake on growth of new industrial sectors expected under bio economy. Bio-based molecules are also forced to present the same purity as molecules provided from petrochemicals industries. Even though considerable progresses on biotechnologies allowed to reach high efficiency conversions, more remains to be done, especially for intensifying purification processes concerning recovery rates and energy efficiency. Membrane separation technologies could be used in association with perfectly mastered technologies as distillation and liquid extraction in order to lead significant process optimizations.

Illustration: Principle of membrane transport



Main results

Confidential

Objectives and stakes

The aim of this work is to take a particular interest in membrane technologies applied to the dehydration of bio-based molecules, where a distillation process could require too much energy. The purification and recovery of solvents used for the separation is also to consider. One of the major issues is to choose the most suitable membrane separation process (as well pervaporation & vapor permeation) from industrial specifications leading to establish a predictive model according to the industrial context. This includes a scale up of an experimental pilot on an industrial site if optimizations results are reached.

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Methodology / Experimental approach

Thermodynamic approach of separation performances to identify and lead the choice of an organic or/and inorganic membrane support. Experimental study at laboratory scale and performance comparison with reference processes. Conception of a pilot plant which could be integrated on a "green chemistry" industrial site. Model establishment and simulation of results to develop a predictive tool for an industrial scale up with a comparative energy evaluation.

2017 	PhD subject : Modeling, simulation, dynamic optimization and nonlinear control of a reactive evaporation process for synthesis and deposition of zinc oxide thin films <p style="text-align: center;"><u>Asdrubal Ramirez (1st year)</u></p> Supervisor 1 Gerardo GUZMAN , Supervisor 2 Abderrazak LATIFI Axe 2 ODCA	
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Keywords: Plasma Assisted Reactive Evaporation (PARE), State estimation, Dynamic optimization, Non-linear control

General context, scientific issues

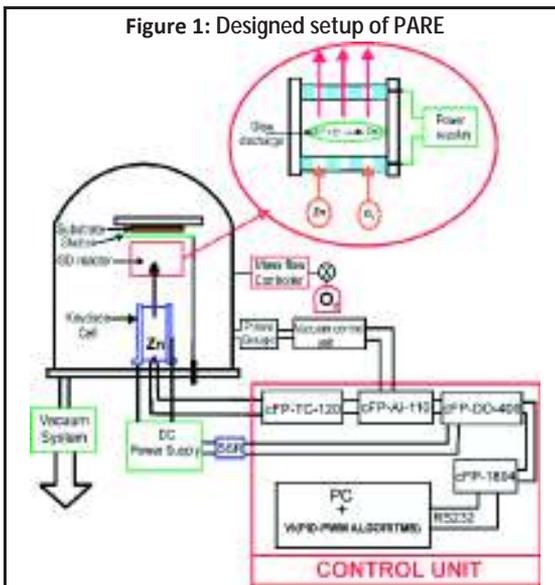
Zinc oxide (ZnO) is a semiconductor material characterized by having many interesting optoelectronic properties such as a wideband gap, a large exciting binding energy of 60 meV and high transparency in the visible region, which has made way for many applications, including flat panel display, light emitting diodes, and solar cells [1-2]. The demand for ZnO thin films has increased in an exponential way in the last 20 years. Various methods, such as RF magnetron sputtering, reactive sputtering, CVD, CBD, spray pyrolysis and sol gel techniques have been used to fabricate ZnO films. Among these methods, magnetron RF-sputtering is considered the most favorable technique for large area deposition and mass production. However, the RF-sputtering deposition process has cost limitations in large-area manufacturing, associated with the use of ceramic targets. In contrast, ZnO deposited by Plasma Assisted Reactive Evaporation (PARE) with Zn as the starting material is in terms of cost and large-scale production better than the RF-sputtering method. Additionally this system allow deposition of thin films of both, i-ZnO and n+-ZnO films due the possibility of change the O₂ density vacancies.

Objectives and stakes

The achievement of the desired performance specifications in the operation of PARE process requires the development of accurate mathematical models that can be used for optimal design of the reactor and flow arrangements and test the performance of different control systems. The key issue in the development of a mathematical model for PARE processes is the understanding of the physico-chemical phenomena complexity, which arises from factors such as glow discharge chemistry, electron density and energy distribution, ion transport, diffusive and convective mass transfer, bulk and deposition reaction kinetics.

Methodology / Experimental approach

The approach adopted here consists of:
 1. Build a dynamic model for a pilot PARE reactor to represent the operating system and to predict the main state variables configuration.
 2. Calculate by means of dynamic optimization the optimal time profiles (flow rates, pressure and



temperature) required in the PARE system to maximize the ZnO thin film production or minimize the batch time, subject to constraints on the final product quality and reactor.

3. Implement state estimators or observers of the state variables such as an extended Kalman filter to be used in the application of a state-space control technique and provide valuable information for monitoring.
4. Develop and implement a nonlinear geometric control strategy using virtual instruments for a pilot reactive evaporation reactor. The selected dynamic state space model will serve to obtain an optimal trajectory, develop the control law, estimate the states and will be used to test the final performance.

Main results

Figure 1 shows a schematic representation of the setup designed and implemented to grow ZnO thin films by PARE. The current works deal with modeling and simulation of PARE and the first results are hopefully expected soon.

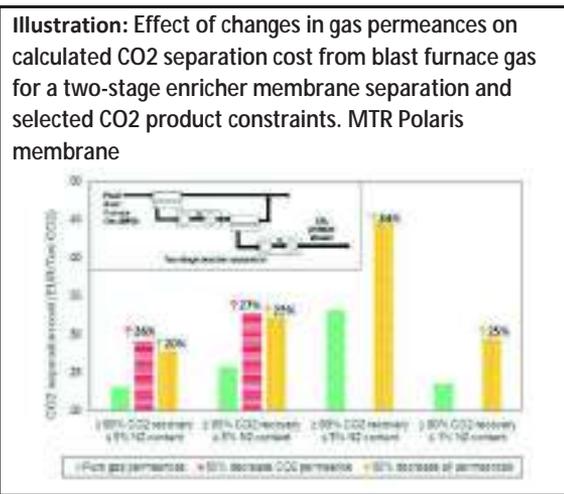
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[1] G. Mo Nam and M. Seok Kwon, Journal of Information Display, 2008, 9, 8-11.
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2017 	Gas Membrane Separation Processes for CO₂ Valorization of Blast Furnace Gas (BFG) <u>Álvaro RAMIREZ SANTOS (4th year)</u> Eric FAVRE, Christophe CASTEL Axe 2 EMSP	
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Keywords: Gas separation, polymer membrane, blast furnace gas (BFG), dense membrane, carbon capture and utilization.

General context, scientific issues
 The Iron and steel sector is the second largest industrial energy user and the largest industrial source of CO₂ emissions. New programs seeking to improve energy efficiency and reduce GHG emissions from the steelmaking industry are studying alternative uses for blast furnace gases in order to reduce emissions. One promising alternative is CO₂ and CO valorization in which emissions are used for the production of valuable products. Membrane gas separation has been proposed as a potential technology for CO₂ separation from steelmaking gases.



Objectives and stakes
 This thesis is carried out within the VALORCO project in partnership with Arcelor Mittal and ADEME. The project aims to reduce total carbon emissions by at least 30%. The objective of this thesis is the conception and design of a gas membrane separation process allowing CO₂ valorization by chemical or biotechnological transformations. Technical feasibility and economic profitability will be evaluated to assess the interest of developing an industrial pilot during the following stage of the project.

Main results
 A literature survey was carried out to determine the state of the art of membrane separation applied to steelmaking gas separation. Membrane permeances for the problem gases were retrieved for 2 commercial membranes: MTR Rubbery membrane and UBE Polyimide membranes. A gas permeation unit was imported into a process simulation environment (Aspen plus) allowing separation studies for diverse architectures. An economic model has been implemented allowing the calculation of separation cost for each architecture considered. Several architectures were evaluated and operation parameters (membrane surface, compression ratio, number of stages) have been optimized to minimize cost for defined separation targets. Gas permeance data was validated at our laboratory-scale permeation unit under mixed-gas conditions.

Methodology / Experimental approach
 Data for two commercially available membranes, a H₂ selective glassy polyimide membrane from UBE industries and a CO₂ selective rubbery composite membrane from MTR Inc. have been used for the simulation of blast furnace gas, coke oven gas and blast oxygen furnace gas separation, first in a one stage process and then in a multistage architecture by means of an in-house developed gas permeation simulation tool exported to the Aspen plus software. Gas permeance was validated at our laboratory-scale permeation unit under mixed-gas conditions and varying temperature and pressure. The effect of operating parameters (pressure ratio, membrane surface, stage cut) on separation performances was studied. Energy and surface requirements are taken into consideration by a cost model implemented within the simulation.

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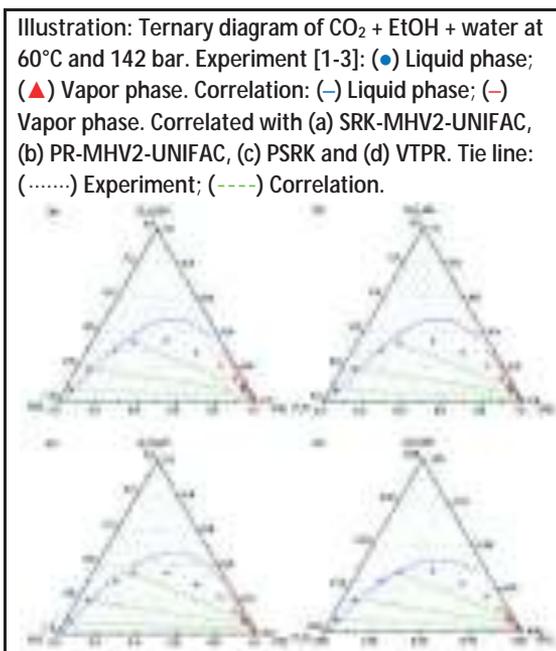
<p>2017</p> 	<p>Phase Equilibrium Study of the Ternary System CO₂ + H₂O + Ethanol At Elevated Pressure for the Supercritical Extraction Of Polar Compounds From Natural Products</p> <p><u>Renan Ravetti Duran</u> (Post-doc')</p> <p>Danielle Barth Axe 2 EMSP</p>	
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Keywords: Vapor-liquid equilibrium; Water/ethanol/CO₂; High pressure; Supercritical extraction

General context, scientific issues
 In recent years, supercritical extraction has been widely studied and applied industrially through its ability to efficiently separate components of low volatility. The most frequently used solvent is carbon dioxide, which is generally mixed with a cosolvent (e.g. ethanol) in order to increase the solubility of polar compounds. In particular, CO₂ + ethanol mixtures are classically used as solvents when extracting biomolecules from natural products. However, natural products usually contain water, which reduces the separation efficiency of the solvent, because of the strong interaction between water and ethanol and between ethanol and CO₂.

Objectives and stakes
 The purpose of this study is to analyze the vapor-liquid equilibrium (VLE) behavior of the CO₂ + ethanol + water ternary system in order to control and even optimize the process of extraction of substances issued from natural resources. The purpose of this study is to select an appropriate thermodynamic model among the ones available in commercial process simulators for representing the phase behavior of the system of interest.

Methodology / Experimental approach
 PRO/II software (Schneider Electric) was used to generate phase diagrams calculated from the two equations of state SRK (Soave-Redlich-Kwong) and PR (Peng-Robinson) combined with the following mixing rules: Panagiotopoulos-Reid (SRKP and PRP), modified Panagiotopoulos-Reid (SRKM and PRM) and Huron-Vidal (SRKH and PRH). All models were tested out on 3 binary systems (CO₂ + ethanol, CO₂ + water and ethanol + water) and 1 ternary system (CO₂ + ethanol + water).



Main results
 The binary CO₂ + ethanol system was studied at 18°C, 40°C and 60°C. The second binary, CO₂ + water, was analyzed at 25°C, 50°C and at 60°C. For ethanol + water system, the VLE behavior was analyzed at 25°C, 40°C and 60°C. Finally, the experimental data for the ternary CO₂ + ethanol + water system were obtained at 40°C and 60°C, under pressure of 101, 142 and 185 bar. It appears that the 3 cubic equations of state Panagiotopoulos-Reid, modified Panagiotopoulos-Reid, Huron-Vidal-NRTL and the non-cubic EoS PPC-SAFT as well could be used to model the phase behavior of the CO₂ + ethanol system but fail dramatically in reproducing the experimental phase diagrams of the CO₂ + water and water + ethanol systems.
 The optimal thermodynamic models for application of interest are MHV2-UNIFAC, VTPR and PSRK models.

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2017

Membrane reactors : Methodological approach in process design



RUIZ VASQUEZ Camilo (Ingénieur de recherche)

Jean-Marc Commenge, Jean-François Portha
Axe 2 | PRISM |



Keywords: Process integration, Reactor-Separator-Recycle, Process intensification, Process design, Coupled unit operations, Membrane separation.

General context, scientific issues

Choosing unit operations is one of the most critical and early steps in process design. They will define the technologies, utilities, control strategy, by products, etc. By this way, choosing the process steps set substantially the OPEX and CAPEX in overall project.

In the other hand, integrated processes, coupled units and intensified equipments have been largely developed in the last decades. Despite they are all used as cost minimization tools, they are not included in traditional process design approach¹.

Objectives and stakes

The main objective of this project is to identify quantitative criteria and/or rules of thumb in order to choose the most interesting operation arrangement even in a very early phase of the process design approach.

To do so, two specific cases are studied: membrane separator in a reactor-separator-recycle loop and its coupled equivalent, a membrane reactor.

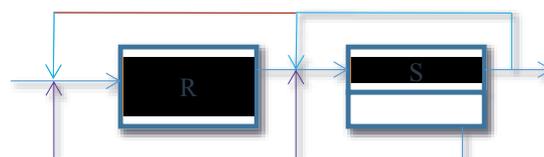
At the end of this research work, an algorithm defining the best superstructure and some optimal operation conditions will be designed.

Methodology / Experimental approach

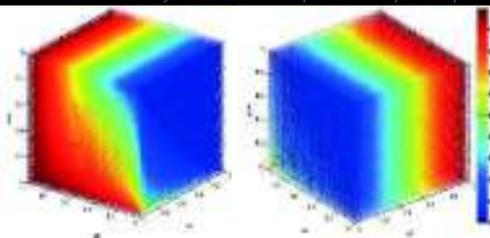
The problem is treated in two stages, the first and simpler one is the study of non-coupled systems presented in the figure. It allows to establish the nature of the decision criteria (numerical, qualitative, economical, technical, etc.) and the basic information needed to make a choice.

The second step will be the study of membrane reactor: it includes the mathematical modeling and characterization of transport and reaction phenomena. In addition the points identified before, output variables or decision criteria must be evaluated in order to guarantee a good comparison. Some industrial case studies will be treated in order to demonstrate the reliability of the algorithm. Finally, most of the work will require numerical and simulation tools, such as MatLab, Proll, and Aspen HYSYS.

Illustration:



Global structure for the reactor-separator-recycle loop.



Optimal efficiencies reached by the reactor-separator-recycle loop.

Main results

In the first instance, the uncoupled case is studied and a technical criterion is chosen: the global efficiency. In this way, an equation to obtain the global efficiency from the local ones is deduced². This equation enables to describe the global performance of all possible structures in the reactor-separator-recycle loop. Some of the global input and output variables to the algorithm have been identified.

In parallel, the first case studies of membrane reactor have been established and equations describing a preliminary performance index have been written for the simplest cases³.

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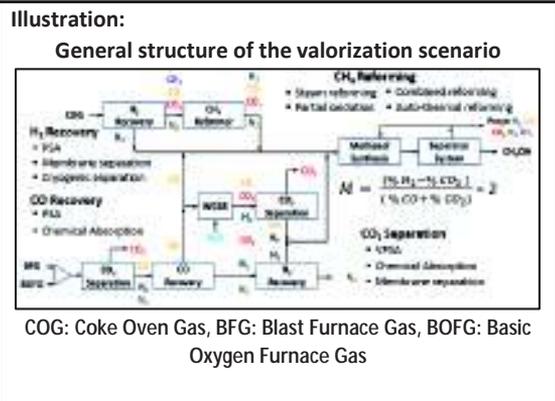
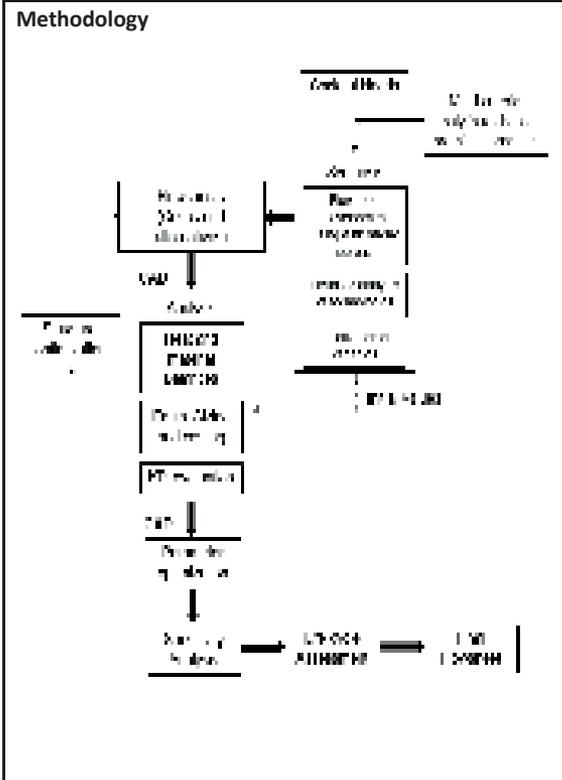
<p>2017</p> 	<p>Conceptual process design for the thermochemical valorization of gases from integrated steelworks</p> <p><u>URIBE-SOTO Wilmar (4th year)</u></p> <p>PORTHA Jean-François, COMMENGE Jean-Marc, FALK Laurent</p> <p>Axe 2 PRIMO</p>	
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Keywords: Steel mill off-gases, Thermochemical Valorization, Water-Gas Shift Reaction, Methane Reforming, Methanol Synthesis, Process Synthesis, Multi-Objective Optimization, Life Cycle Assessment, Green Process, Heuristic Design, Simulation, Parameter Sensitivity Analysis.

General context, scientific issues

The steel industry is the main generator of CO₂ among different industrial sectors. In this context, the VALORCO (VALOrization and Reduction of CO₂ emissions in the industry) project was launched. The VALORCO project considers different pathways of CO₂ valorization through its transformation into high added value products. This particular study focuses on the conception of a thermochemical valorization pathway of off-gases from integrated steelworks.

- Objectives and stakes**
- The identification, evaluation and comparison of the valorization pathways,
 - The design and optimization of the selected process,
 - The assessment of environmental impacts associated to the valorization pathway using at life cycle approach.



Main results

Several products can be synthesized from the available gases: 10 products have been identified as the most promising paths. After a multi-criteria analysis just two products were kept: methanol and urea. A new more elaborate multi-criteria analysis conducted to the selection of methanol as the most promising path.

A review of several alternatives proposed during last years to valorize the available gases was accomplished, thus allowing the development of a general structure using a hierarchical approach. This structure condenses different process flowsheets for the thermochemical valorization of available gases. A heuristic analysis was realized to choose the best recovery and separation processes. The studied scenario includes the possibilities of hydrogen generation, using Methane Reforming (MR) or Water-Gas Shift Reaction (WGSR). A review of technologies to carry these processes on an industrial scale was achieved. A thermodynamic analysis of these reactions was carried-out to find in a first approximation the values of operating conditions.

Future works will aim at optimizing the process flow-sheet and at defining the most promising process in terms of economic and environmental impact.

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2017



Evaluation of the potential of hollow fiber composite membrane contactor for the chemical absorption of CO₂ from flue gas and the regeneration of the chemical solvent

Kévin Villeneuve(3rd year)

Denis Roizard, Sabine Rode
Axe 2 | EMSP



Keywords: CO₂ Capture, Membrane contactor, Absorption, Desorption

General context, scientific issues

Global warming is among the main issues of our century. Post-combustion CO₂ capture is an option to reduce greenhouse gases emissions. A way to achieve this purpose is chemical absorption of CO₂ in chemical solvents. Within that frame, thanks to the high interfacial area provided, Hollow Fiber Membrane Contactors (HFMC) present a promising intensification potential compared to conventional gas-liquid packed column. [1]. Composite membrane (i.e. a dense polymeric skin coated on a porous support) is used in order to prevent membrane wetting due to liquid penetration into the pores [2].

Objectives and stakes

- Study of the potential of the technology for the absorption and desorption of CO₂ at lab scale.
- Modelling of the process by taking into account the heat transfer and the multi-component mass transfer of both CO₂, solvent and water.
- Simulation of the process within industrial relevant conditions.
- Assist the development of a pilot scale demonstrator within industrial context (material selections, sizing, and results analysis).

Methodology / Experimental approach

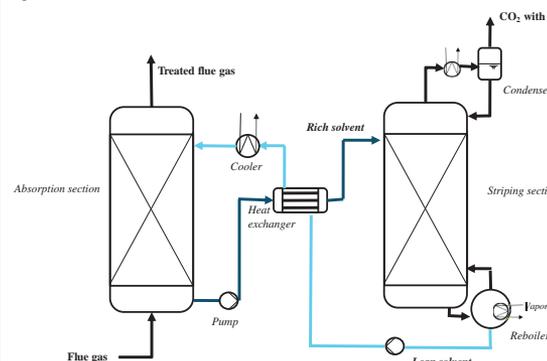
Experiments:

- Lab scale pilot were used to vary absorption conditions in order to get stable performances.
- Membrane ageing were performed within stripping conditions (high temperature and pressure).
- Desorption lab pilot with membrane contactor used for concept validation and determination of the advantages and drawbacks of the technology.

Modelling

- 1D adiabatic modelling of the CO₂ absorption membrane contactor in the Aspen Custom Modeler® Environment.

Illustration: Process diagram of CO₂ capture by chemical absorption (packed columns can be replaced by HFMC).



Main results

Experiments:

Industrial relevant conditions were found to maintain stable capture efficiency when using membrane contactor.

Study of the desorption step is still on-going.

Modelling:

Experimental and simulation results are in good agreement.

Simulations study reveals that volume reduction of the unit when compared to packed column can be obtained. In some extent and depending on the membrane material, reduction of the solvent leaks can also be expected.

Nevertheless, within industrial condition, condensation of water is likely to occur and it may lead to membrane wetting even for composite membrane.

Wetting by water condensation in the pores is currently on study (experimental and modelling).

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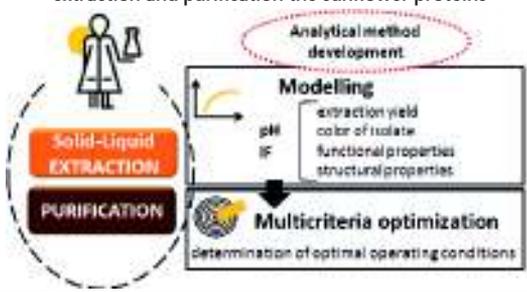


BIOPROMO

BIOPROCESS AND BIOMOLECULES

2017 	Development and optimization of an extrapolable process to production protein isolates from sunflower meals <u>Sara Albe Slabi (2nd year)</u> Kapel Romain, Mathé Chistelle Axe 3 BioProMo Avril SCA	
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Keywords: sunflower cake, protein, extraction, purification, ultrafiltration, size exclusion chromatography, phenol, quantification, modelling, optimization

<p>General context, scientific issues Nowadays, the world's population constantly increases. Consequently, the worldwide consumption of proteins for human nutrition is also increasing. So there is a strong need in new sources of proteins to fulfill these needs. Sunflower is a plant widely grown in Europe for edible oil. After extraction, a by-product (cake) rich in protein is released. At present this sunflower cake is used in animal nutrition, but the qualities of proteins might be suitable for human nutrition [1-3].</p>	<p style="text-align: center;">Strategy of modelling and multicriteria optimization of extraction and purification the sunflower proteins</p> 
<p>Objectives and stakes The main bottleneck for the industrialization of proteins production lies on the poor extractability and the green colored of the products due to binding of phenolic compounds to proteins [1-3]. The objective of this project is to develop and optimize a process that produce colorless protein isolates with functional and nutritional properties preserved at a satisfying yield.</p>	<p>Main results In order to characterize quickly and precisely the protein and their concentration in aqueous extract a method by size exclusion chromatography (SEC) was developed. In comparison to reference method according Kjeldahl, SEC is automatic and time-saving. It is a crucial step for the modelling and optimization approach which requires a lot of analysis. The first design of experiments using hexane defatted sunflower meal was achieved. The effect of pH and ionic strength on protein extractability, solubility and phenolic contamination was investigated. It proves the necessity to use salt in order to both increase protein yields and limit protein-polyphenol interaction. However, addition of salt results in poor solubility of protein isolate and increase of cost of production. The results clearly showed that extraction yield cannot reach the yield target value. It is probably due to denaturation of protein under heat treatments during oil extraction process (desolventization step). The whole methodology is currently applied with cold-pressed sunflower meal without solvent deoiling.</p>
<p>Methodology / Experimental approach</p> <p>Modelling and multicriteria optimization of extraction process The goal of this part is the identification of optimal conditions for protein extraction from sunflower cake. For this purpose, design of experiments will be achieved in order to study the impact of pH and ionic strength on extraction yield, color of powder and condition of functional and structural properties of isolate. Conditions selected by multi-criteria optimization will be retained for the next stage of project.</p> <p>Modelling and multicriteria optimization of purification process Subsequently, the study of purification process of aqueous extract using membrane ultrafiltration will be carried out. The objective is to maximize the process performance in term of purification yield, purity and color of isolate.</p>	<p>References [1] Pickardt C. et al., Optimisation of mild-acidic protein extraction from defatted sunflower (<i>Helianthus annuus</i> L.) meal. <i>Food Hydrocoll.</i> 23 (2009) 1966-1973; [2] Gonzalez-Perez S., et al., Sunflower proteins: overview of their physicochemical, structural and functional properties. <i>J. Sci. Food Agr</i> 87 (2007) 2173-2191. [3] Pickardt, C. et al., Pilot plant preparation of light-coloured protein isolates from de-oiled sunflower (<i>Helianthus annuus</i> L.) press cake by mild-acidic protein extraction and polyphenol adsorption <i>Food Hydrocoll.</i> 44 (2015) 208-219.</p>

<p>2017</p> 	<p>Improvement of rapeseed albumins digestibility and functionalities by enzymatic proteolysis</p> <p><u>Sophie Beaubier (1st year)</u></p> <p>Romain Kapel, Irina Ioannou Axe 3 BioProMo Avril SCA</p>	
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Keywords: Rapeseed albumins, hydrolysis, enzymes, digestibility, peptides, functionalities, optimization, chromatography

General context, scientific issues

Rapeseed albumins extracted from meals have a well-balanced aminogramme and are rich in sulfur-containing amino acids, which is rare for plant proteins. Researches also show particularly interesting functionalities [1]. However, this protein presents a poor digestibility because of its gastro-intestinal proteolysis resistance, what limits its industrialization in human nutrition [2]. Enzymatic proteolysis is used to improve proteins digestibility, their techno-functional properties and to release bioactivities such as antioxidant or antimicrobial properties. The criterion improvements are dependent on the hydrolysis degrees (DH).

Objectives and stakes

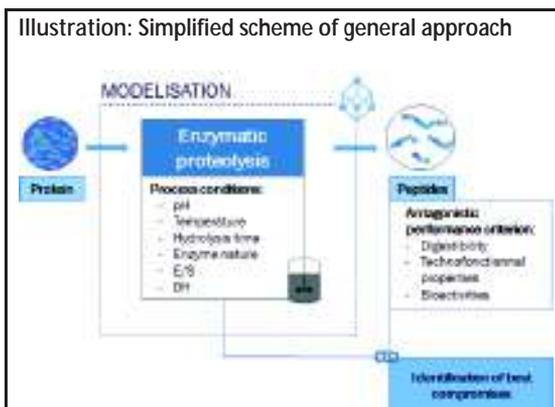
The main objective of this project is to highlight process conditions of enzymatic proteolysis of rapeseed albumins allowing to solve the problem of digestibility of these proteins while maintaining, even improving, their functional properties (emulsification and foaming capability) and bioactivities (antioxidant and antimicrobial). However, many operating conditions (choice of the protease, pH and T, ratio E/S and progress of the reaction) are to be considered, which constitutes a strong scientific bottleneck.

Methodology / Experimental approach

A strategy of modelling the effect of the operating conditions (pH, T, E/S, DH) on each performance criterion (digestibility, functionalities and bioactivities) by experimental design will be realized for every chosen protease. Evaluation of criterion will be done by means of *in vitro* systems.

The model equations linking operating conditions and performance criterion will allow to choose the protease and proteolysis conditions the most favorable to improve the digestibility and functionalities and/or generation of the most active hydrolysates.

The process conditions of enzymatic proteolysis will be extrapolated on a scale (10 L) which allows the validation of properties with real systems.



Main results

Analytical methods development:

Quantification of the number of peptides bonds cleaved at a given moment of the hydrolysis (or DH) represents an interest for the control of enzymatic proteolysis. In addition, the molecular size of generated peptides plays a major role in digestibility and functional properties. It's important therefore to determine this criterion as there is no existing reliable method to date.

Hence, an original method of determination of DH by Size Exclusion Chromatography, based on a recently published method [3], and quantification of the average number of amino acids by peptide is currently developed. This method will be used to study the *in vitro* digestibility after a simulated gastro-intestinal digestion.

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2017 	Identification of factors at the origin of the phenomenon of beer gushing and development of a premature detection technique of the gushing risk <u>Julien Billard (4th year)</u> Ivan Marc, Romain Kapel Axe 3 BioProMo CIFRE - Institut Français des Boissons de la Brasserie et de la Malterie	
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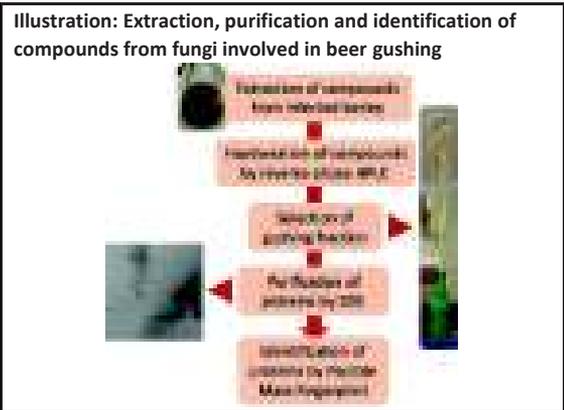
Keywords: beer gushing, barley, malt, fungus, fractionation, chromatography, electrophoresis

General context, scientific issues
 The gushing of beer is an over-generation of foam more or less explosive following the opening of a bottle without prior agitation. The leading cause of this problem which becomes increasingly frequent is the fungi contamination of barley and malt. Currently, there are few data on the compounds involved but some low molecular weight hydrophobic proteins (7 kDa) active at very low concentration have been described to be responsible in the gushing phenomenon [1].

Objectives and stakes
 The thesis objectives are to identify all compounds involved and/or at the origin of the beer gushing. Once identified, the point is to:

- determine their origin : from seed, fungi or an association between their two sources
- develop a premature method of detection,
- study their evolution during brewing process.

Methodology / Experimental approach
 These compounds are currently searched in malt extract naturally contaminated and barley artificially contaminated by fungus. Their compounds, at the surface of barley and malt, are produced by some fungus involved in the gushing phenomena [2].
 Two methodologies of active gushing compounds research are developed: (1) a macroscopic analysis of raw material to find some difference between gushing and non-gushing samples by various methods (HPLC, SDS-PAGE, MS), and (2), their fractionation with separate technics (membrane processes and chromatography) to concentrate / purify the effective gushing compounds and to determine their gushing power. Finally, compounds with gushing activity are identified by peptide mass fingerprint with MALDI-TOF.



Main results
 An extraction of compounds at the surface of barley is performed with ultrapure water. This extract is fractionated by high performance liquid chromatography. The first step is to verify the possibility to reduce volume to preserve a significant gushing potential (higher than 30 g in beer) to purify it by HPLC. The second one, is to verify that this technic preserves the gushing potential. If so, we then fractionate the profile with semi preparative column and analyze the gushing potential of each fraction. Three fraction are analyzed (1) a fraction which contains carbohydrate and non-protein nitrogen, (2) a fraction which contains protein with high absorbance at 280 nm and (3) a fraction which contains protein with a low absorbance at 280 nm. Only the third fraction has a gushing activity. As the protein content is complex, we decide to separate protein by two dimensional electrophoresis (2DE). Then separate spot are analyzed by peptide mass fingerprint after a trypsin digestion. In our proteins, we have found an other protein from the family of cerato platanin with properties close to hydrophobin. According to their properties, this protein excreted by fungus at the surface of barley could be involved in gushing.

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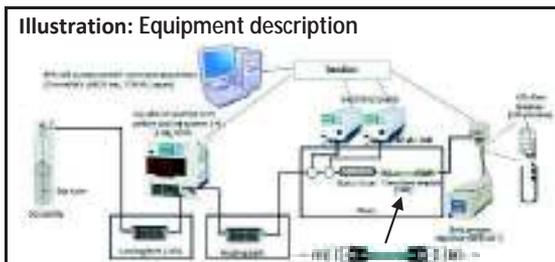
2017 	PhD subject: Intensified & sustainable enzymatic acylation processes on innovative macroporous/mesoporous materials <u>Mohamed Chafik BOURKAIB (1st year)</u> Supervisor 1 Isabelle CHEVALOT, Supervisor 2 Yann GUIAVARC'H Axe 3 BioProMo	
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Keywords: Enzymes, acylation, supercritical CO₂, immobilized enzyme

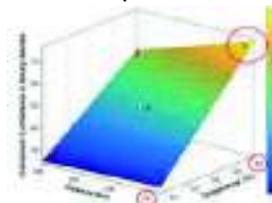
General context, scientific issues
 The N-acylation of amino acids and peptides which consists in grafting an acyl donor (fatty acid) onto the amino group of an acyl acceptor (amino acids or peptides) is currently carried out at an industrial scale via the reaction of Schotten-Baumann for the production of lipoaminoacids (LAA) largely used in cosmetics and pharmaceuticals. Despite its good performance this chemical reaction unfortunately requires the use of acyl chloride, organic solvents and a high pH with salts generation, which is an environmental issue. In this context, the development of soft biological processes using enzymes is considered as a potential alternative, especially since studies reported by Zaks and Klibanov [1] demonstrating that lipases in anhydrous media can have a synthetic activity (acylation) instead of a hydrolytic activity. Since then efforts were put on the use of various non-aqueous media such as organic solvents, ionic liquids, eutectic solvents as well as supercritical CO₂ (scCO₂).

Objectives and stakes
 Because N-acylation in supercritical CO₂ is quite difficult due to amino acid solubility limitations the optimal operating conditions for immobilized *Candida antarctica* lipase B (CALB) under scCO₂ were firstly determined for the production of geranyl acetate (O-acylation),
 -another goal is to evaluate the N-acylation activity and stability of home-produced immobilized enzymes on macro/mesoporous siliceous supports such as described by Backov in 2012 [2],
 -the final objective is to generate a competitive green process for the production of LAA.

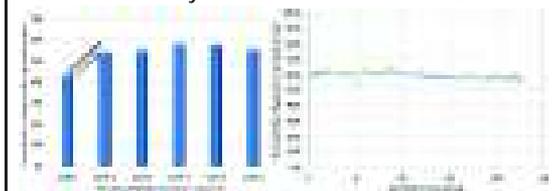
Methodology / Experimental approach
 In order to evaluate the activity/stability of the CALB immobilized on macroporous beads we studied the potential of Lipozyme 435 (Novozymes, Denmark) to produce geranyl acetate from acetic acid and geraniol in a packed bed reactor (PBR) using scCO₂ as a solvent. The equipment used is shown below. Different conditions of pressure and temperature (following a DoE) and different PBR configurations were used.



Main results
Design of experiment: positive and negative effects of temperature and pressure, respectively, on the enzyme activity. Best activity observed at 65°C and 150 bar with turn over number of 1 and 75 % conversion in 8 s average residence time (30 min runs with n=3).



PBR configurations: Because of water accumulation along the PBR, competitive hydrolysis was observed, especially when using long PBR instead of short PBR, which led to lower geranyl acetate yields. At 55°C and 200 bars, using two short reactors of 300 mg beads each in parallel instead of one long reactor of 1500 mg beads, led to 75 % conversion instead of 73 % conversion, respectively, showing the importance of water content control and residence time on process efficiency.
Stability test: The very good stability observed over pressurisation/depressurisation cycles and also over a single long 22h run confirmed the potential of lipase when used in anhydrous solvent such as scCO₂



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<p>2017</p> 	<p>Succinate production by <i>Corynebacterium glutamicum</i>: from metabolic modeling to dynamic optimization</p> <p><u>Amani BRIKI (1st year)</u></p> <p>Stéphane DELAUNAY , Eric OLMOS, Frantz FOURNIER Axe3 BioProMo</p>	
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Keywords: metabolic modelling, simulation, aero-anaerobic process, *Corynebacterium glutamicum*, succinate

General context, scientific issues

Succinic acid is a diacid used nowadays as a building block in the synthesis of various molecules of interest. It can be produced by chemical or biological synthesis. For a few years, a part of succinate is industrially produced using a microbiological process. *Corynebacterium glutamicum* is industrially used for decades for the production of amino acids such as glutamate and lysine. Previous studies proved its ability to also produce several organic acids including succinate. While bacteria growth is related to an aerobic process, the succinate production depends on both a low level oxygen supply and the glucose consumption currently described by the ratio Oxygen Uptake Rate/Glucose Uptake Rate (OUR/GUR, 1). However, the influence of this ratio remains to be elucidated at both metabolic and process levels.

Illustration: experimental setup to study the influence of OUR/GUR ratio on the succinate production by *C. glutamicum*



Objectives and stakes

The goal of this study is first, to understand the impact of such extracellular environment on the metabolic regulations. This first step of the work requires a metabolic model describing the intracellular fluxes using a Flux Balance Analysis (FBA) approach. Then, this metabolic model should be coupled with a macro-kinetic model to allow the simulation of the time-variations in the intracellular fluxes during the succinate production process. This coupling will give clues for the dynamic multicriteria optimization of the succinate production using *C. glutamicum*.

Main results

As no existing metabolic model was able to predict the behavior of *C. glutamicum* during the growth and succinate production, a simplified model was first built using FBA (OptFlux software). This model was validated for the culture of a wild-type strain of *C. glutamicum* in anaerobic conditions (for organic acid production). Using the previous experimental data on the succinate production by *C. glutamicum* (2), it was shown that the succinate production occurred for an OUR/GUR ratio less than 1. An increase of the succinate production was measured when this ratio was decreased. However, in these experiments, the lowest value of OUR/GUR was 0.5, which remains higher than the optimal value of this ratio for the succinate production (1). Some continuous cultures were therefore conducted to explore the influence of weak OUR/GUR ratios on the organic acids production. These experiments are still in progress.

Methodology / Experimental approach

As metabolic modeling is the heart of this study, the methodology consists in alternating numerical modeling and experimental steps. Some existing metabolic models are first modified according to the genetic properties of the selected strain. Experimental results collected during previous discontinuous and fed batch cultures (2) are then completed by continuous cultures to explore the influence of environmental conditions. The performances of the succinate production process are determined in measuring organic acids concentrations, substrate conversion, yields, and carbon yields with respect to oxygen and glucose consumption rate.

References

- (1) Shinfuku, Y., Sorpitiporn, N., Sono, M., Furusawa, C., Hirasawa, T., and Shimizu, H. *Microbial cell factories*, (2009) 8-43.
- (2) Kaboré, A.K., Olmos, E., Fick, M., Blanchard, F., Guedon E. and Delaunay, S. *Process Biochemistry*, 52 (2017) 10-21.

2017



Biofuels and building blocks production by anaerobic fermentation of thermally pretreated cellulose

BUENDIA, Felipe (Third Year)

Emmanuel Guedon¹, Anthony Dufour² | Axe 3
¹Bioprocesses-Biomolecules, ²Kinetics-Thermodynamics



The global demand of energy and services is growing continuously despite the decrease in oil reserve availability. In addition, the use of fossil carbon sources generates billions of tons of CO₂ releases into the atmosphere. A replacement source is now required. Lignocellulosic biomass presents an interesting alternative, as renewable carbon based energy sources, which respects to the environment. This project seeks the valorization of cellulose and derivatives through an efficient coupling of cellulose thermochemical conversion and fermentation

Objectives and stakes

- Coupling the thermochemical conversion of cellulose with a fermentation process.
- Cellulose valorisation into profitable chemicals and/or biofuels.

Methodology/ Experimental approach

This work has two stages:

- In order to obtain soluble oligosaccharides from cellulose, various techniques of thermochemical conversion will be implemented.
- Biological transformation will be performed by fermentation of carbon substrates obtained in the previous step.



Thermochemical conversion

- Pyrolysis
- Liquefaction
- Extrusion
- Analysis: HPAEC-PAD

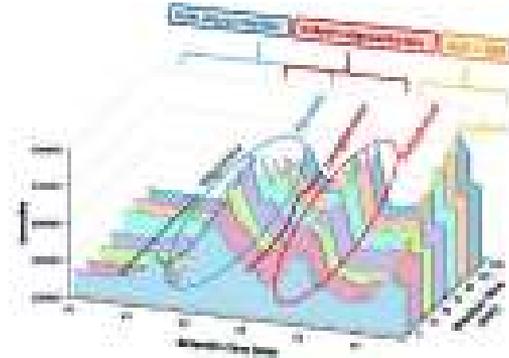


Batch Fermentation

- Growth kinetics
- Metabolite analysis: HPLC-UV-RID, GC-TCD

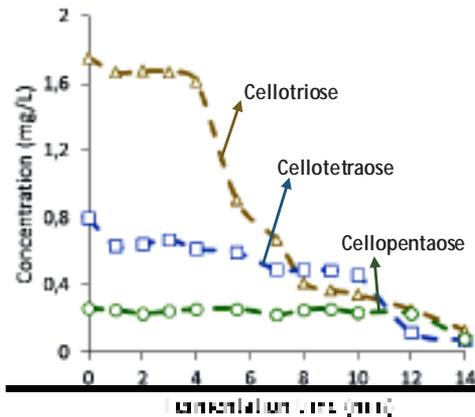
Main Results

Different products identified after cellulose liquefaction in hot-compressed water:



Mass spectra of soluble products obtained by SEC*SEC-MS

First evidence of the fermentation of a mixture of oligosaccharides by *Clostridium acetobutylicum* [1]:



Kinetic consumption of cellulose derived oligosaccharides during *C. acetobutylicum* batch fermentation

References

- [1] Buendia-Kandia, Felipe et al. "Batch fermentation of d-glucose/cellobiose mixtures by *Clostridium acetobutylicum* ATCC 824: energetic and carbon source regulation. « in « Green process engineering (GPE 2016).

2017



Kinetic study and modeling of the effects of heat treatments and the physico-chemical environment on the degradation and antioxidant activity of flavonoids

Hind CHAABAN (5th year)

Mohamed Ghoul , Irina Ioannou
Axe 3 | BioProMo

Keywords: Flavonoid, degradation kinetic, antioxidant activity, modeling, kinetic parameters, thermal stability, photostability, degradation products

General context, scientific issues

Flavonoids are antioxidants of great interest in the food industry. They are known for their biological activities and thanks to these activities, flavonoids have protective effects on human health [1]. However, the human diet consists in formulated products. Thus, it is necessary to take into account the effect of food processes and the effect of the physico-chemical environment on the flavonoid degradation and on the evolution of their antioxidant activity.

Objectives and stakes

The objective is to study and model the effects of temperature, light and oxygen on the flavonoid degradation and the evolution of their antioxidant activity. For this : (i) degradation kinetics were plotted and modelled for heat and light treatments, (ii) evolution of antioxidant activity was determined, (iii) relationships between structure, stability and antioxidant activity were determined according to the study of 6 flavonoids with different structure and (iv) the identification of the degradation products structure was realized.

Methodology / Experimental approach

Flavonoids chosen belong to four classes of flavonoid with structural differences. Rutin (flavonol), naringin and eriodictyol (favanones), mesquitol (flavone), luteolin and luteolin 7-O glucoside. In order to establish relationships between flavonoid structure-stability and antioxidant activity, the following methodology was applied:

- 1- Study the effect of thermal processes on flavonoids: Experiments were carried out with two heating modes:
 - 1.1 Isothermal conditions (oil bath) corresponds to a heating at a fixed temperature during a given time: degradation kinetics were plotted and modeled, kinetic parameters were calculated, determination of the evolution of the antioxidant activity.
 - 1.2 Non-isothermal conditions (microcalorimetry): corresponds to a heating according to a gradient of 4°C per hour. Heat capacities (ΔC_p) were measured and kinetic parameters were calculated.
- 3- Study the effect of the physico-chemical environment: The effect of time, light and oxygen were studied. Degradation kinetics were plotted and evolution of the antioxidant activity was determined.
- 4- Identification of the structure of the degradation products of flavonoids by mass spectrometry.

Illustration: Effects of heat treatments and the physico-chemical environment on flavonoids



Main results

Thermal treatment: The results obtained for the thermal treatment under isotherm conditions indicate that the glycosylated flavonoids are more resistant than the aglycon flavonoids. Results under non-isothermal conditions (in water and water with 10% propylene glycol) confirm those obtained in isotherm conditions. We notice that the addition of 10% propylene glycol leads to a protective effect that delays the thermal degradation of flavonoids.

Treatment with light: The kinetics of flavonoid degradation are strongly influenced by the presence of light. Degradation depend on the structure of the molecules studied. The presence of a hydroxyl group at position 3 and a C2-C3 double bond reduces the stability of the flavonoids [2]. The effect of oxygen is low on the kinetic degradations.

The antioxidant activity: the evolution of the antioxidant activity of the flavonoids was measured during a heat treatment and with different physico-chemical environments. Despite the significant degradation of the flavonoids, the solutions still have an antioxidant activity [3]. This would be due to the degradation products generated. Different evolution were noticed according to the degradation factor and the flavonoid structure.

Identification of degradation products: Degradation products of quercetin, rutin and eriodictyol were identified during a thermal process and during oxidation. Different degradation pathways were identified according to the degradation factor and the flavonoid structure.

References

- 1- Shin, J.E., Kim, J.M., Bae, E.A., Hyun, Y.J., Kim, D.H., I
- 2- Ramešová, S., Sokolová, R., Degano, I., Bulíčková, J., Žabka, J. & Gál, M. (2012).
- 3- Buchner, N., Krumbein, A., Rhon, S., & Kroh, L. W. (2006).

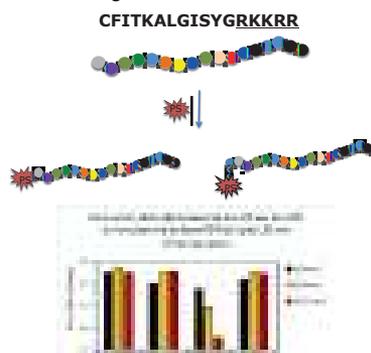
<p>2017</p> 	<p align="center">Targeted PhotoDynamic Therapy</p> <p align="center">Ludovic COLOMBEAU (Postdoc)</p> <p align="center">Céline Frochot – Régis Vanderesse Axe 3 BioProMo - LCPM</p>	
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General context, scientific issues

- Recent research in Photodynamic Therapy is focused on novel techniques to enhance tumor targeting of anticancer drugs and photosensitizers (PS). Coupling a vector to PSs or using nanoparticles could allow a better targeting of receptors that are overexpressed on the surface of tumor cells or on neovessels.

- Treatment of glioblastoma multiform (GBM) is one of the most challenging problems. Despite advances in neurosurgery and radiotherapy the prognosis for patients with GBM, life expectancy at five years is not higher than 10%. PDT offers a localized treatment approach in which improvements in local control of malignant cerebral gliomas may result in significant improved survival.

Illustration: Photosensitizer-peptide targeting LRP-1 for PDT against GBM



Objectives and stakes

- **Project 1:** Photosensitizers coupled to folic acid or antifolate^[1].
- **Project 2:** Photomolecular beacon targeting LRP-1, activable by the MMPs to handle the glioblastoma by photodynamic therapy^[2].
- **Project 3:** AGuIX® or Gold theranostic nanoparticles for vascular-targeted interstitial photodynamic therapy of glioblastoma^[3].

Main results

- **Project 1:** Folic acid conjugates with 7 different photosensitizers (a patent is in progress) and 3 antifolate conjugates with a porphyrin have been synthesized, purified, characterized and their photophysical properties studied. The evaluation of the conjugates' photostability and biological studies are in progress.
- **Project 2:** Peptides described in the literature targeting LRP-1 receptor and peptide-photosensitizer were synthesized and characterized. Because of the poor solubility of the compounds, new peptides and peptide-photosensitizer has been synthesized and the first biological results are performed.
- **Project 3:** Nanoplatfoms targeting NRP-1 have been designed. Their affinity for NRP-1 have been evaluated. The *in vivo* selectivity, evaluated using a skinfold chamber in mice, confirm that the nanoparticles are localized in the tumor vessel wall.

Methodology/ Experimental approach

Organic synthesis methodology:

- Photosensitizers synthesis (LRGP used the Lindsey's methodology under boron trifluoride catalysis),

- Peptides synthesis (All the peptides are synthesized on an automatic peptide synthesizer by fluorenylmethoxycarbonyl (Fmoc) chemistry at LCPM),

- Coupling reagents (DCC, EDC, HATU, HBTU).

- Functionalization of nanoparticles

Characterization techniques:

HPLC / MS / LC-MS / RMN / DLS / Zeta potential...

Photophysical characterization:

UV – visible absorption / fluorescence emission / singlet oxygen formation / steady state and time-resolved

Biological studies (in CRAN, UMR 7039 CNRS-UL):

Uptake, dark cytotoxicity, selectivity, phototoxicity, PDT effects...

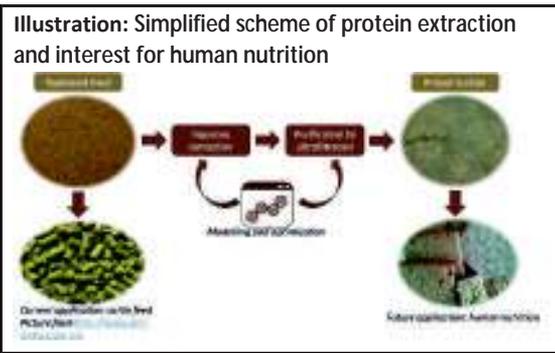
References

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- [2]Stallivieri et al., *J. Med. Chem.*, under corrections.
- [3]Thomas et al., *Biomat*, submitted.

<p>2017</p> 	<p>Development and optimization of an extrapolable process to produce albumin and globulin isolates from rapeseed meals</p> <p><u>Claire Defaix (2nd year)</u></p> <p>Romain Kapel, Frantz Fournier Axe 3 BioProMo Avril SCA</p>	
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Keywords: Rapeseed meal, protein extraction, purification, chromatography, ultrafiltration, multicriteria optimization, modelling

General context, scientific issues
 Nowadays, a major demographic issue has emerged: to feed the increasing world population. More proteins are needed and could be provided by plants, as a complement to meat. To this day, rapeseed meal has been used as a commodity for feed applications. However, this agro-resource is rich in proteins (35%). An industrial process should allow the extraction of these proteins of interest for human nutrition (with a good amino acid profile) and for their properties such as emulsification and foaming capability [1].



Objectives and stakes
 Two main challenges are to be overcome:
 * The first one is to increase the protein extraction yields: so far, only 25 to 30% of the total proteins are recovered. This will be achieved by (i) applying an original strategy for optimizing the extraction step and (ii) by using innovative enzymatic treatments. The remaining part of the extract is composed of anti-nutritional factors, such as phenolic compounds, altering the taste and colour of the final product.
 * The second challenge will be to optimize a membrane based purification process in order to reach the protein isolate quality (purity over 90 %) at a minimum water cost and with the best techno-functional properties.

Main results
 * **Protein extraction**
 During preliminary experiments, it was shown that albumins, one of the two main types of proteins, can be extracted selectively at pH between 2 and 4. As a consequence, a design of experiment was achieved to model this extraction with two factors: pH (2-4) and ionic strength (0-0.5 M) as both influence protein solubilisation. The results showed that the use of salts decreases the selectivity of the extraction while it also increases the total protein yield.
 * **Development of analytical methods**
 An analytical method using an HPLC (High Performance Liquid Chromatography) system combined with size-exclusion stationary phase has been successfully developed in order to identify and quantify the extracted proteins.
 * **Purification by ultrafiltration**
 The cut-off points of the membranes have been determined according to their capability to separate the proteins from the phenolic compounds. Operating conditions are: transmembrane pressure of 2 bars, at room temperature, with a tangential flow of 0.03 mL/(min.cm²), and NaCl salt at 0.05 mol/L.

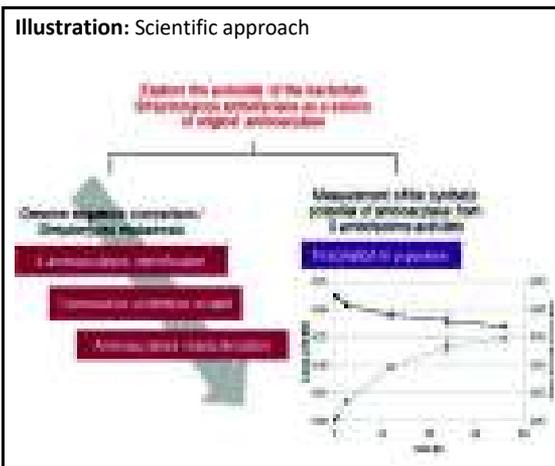
Methodology / Experimental approach
 * **Extraction**
 A multicriteria optimization strategy will be applied in three steps: (i) modelling the effect of the operating conditions on the process performance (protein yield, protein structure, phenolic complexation, protein functionality, powders colour) and extract composition, (ii) define Pareto zones using a diploid evolutionary algorithm [2], (iii) apply decision-making strategies to select the best trade-off operating conditions.
 * **Purification (Ultrafiltration)**
 Development of a strategy to predict the purification performances (yield, purity, productivity) according to the operating conditions and to the composition of the extracts used. This model will be based on mass balance equations [3].

References
 [1] Nioi, PhD thesis, 2013, 219p
 [2] Muniglia *et al.*, European Journal of Operational Research, 153, (2004), 360–369
 [3] Ghodsvali *et al.*, Food Research International 38 (2005) 223–231

2017 	PhD subject : Development of an intensive process for the enzymatic acylation of peptides and amino acids by a multi-scale approach <u>Dettori Léna (3rd year)</u> Chevalot Isabelle, Yann Guiavarc'h, Stephane Delaunay, Catherine Humeau, Xavier Framboisier Axe 3 BioProMo	
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Keywords: aminoacylase ; actinomycetes ; *Streptomyces ambofaciens* ; acylation, enzymatic synthesis, N-oleoyl-lysine

General context, scientific issues
 Peptides and amino acids can be acylated to produce bio-surfactants exhibiting many properties with potential applications as therapeutic, cosmetic and nutraceutical agents. Currently, chemical acylation shows limitations concerning the reaction selectivity and environmental safety. An alternative to this chemical method is the use of enzymes allowing the catalysis of such acylation reactions. Several couples of enzymes and related solvents have already been described. However, the reaction performances of these systems remain limited. There is a need for more fundamental studies of the factors influencing the reaction, based on a more rational approach



Objectives and stakes
 To develop a strategy of intensification concerning process for enzymatic acylation of peptides and amino acids by a systematic approach in order to describe phenomena at different scales

Main results
 The presence of aminoacylase activities was investigated in a crude extract of *Streptomyces ambofaciens*. Two aminoacylases catalyzing the hydrolysis of N-acetyl-L-lysine have been identified in *S. ambofaciens* ATCC23877. The first one has the propensity to hydrolyze the α -amide bond of N- α -acetyl-L-lysine, whereas the second one catalyzes mainly the hydrolysis of N- ϵ -acetyl-L-lysine. These two enzymes were the source of most of the hydrolytic activity of *S. ambofaciens* crude extract. However, a probable existence of at least two other aminoacylases potentially able to catalyze the hydrolysis of N- α/ϵ -acetyl-L-lysine has been highlighted. These last enzymes could also be responsible for the interesting acylation activity that was determined with lysine, SYK or LQKW as acyl acceptors. Indeed, CALB was able to catalyze acylation only on the ϵ -position [1], whereas the crude extract from *S. ambofaciens* possessed the rare ability to catalyze the N-acylation on the α -position of the lysine or of the amino-acid in N-terminal position of peptides, preserving the functional side chains of any amino acids or peptides. This would broaden the perspectives of enzymatic acylation of bioactive molecules with enzymes exhibiting original selectivity.

Methodology / Experimental approach
 Development of strategies for the intensification of peptide acylation reaction at different scales:

- Molecular scale modeling of reaction mechanisms by molecular modeling approach, predicting the regio-selectivity of lipase B of *Candida antarctica* (CALB) and Investigation of the causes of this regio-selectivity by the determination of interactions energies
- Reaction scale: Study of reaction kinetics which depend on the nature of the biocatalyst and its environment (anhydrous solvents such as organic, ionic or deep eutectic solvents and supercritical CO₂, or aqueous environments such as oil in water emulsions). The acylation ability and selectivity of new biocatalyst is also explored.
- process scale: to develop processes with improved performances (assisted by microwaves or microfluidic reactors) and to immobilize enzymes on silica beads in order to recycle them and increase their structural stability

Results presented in this summary only concern research of new biocatalysts

References
 [1] Ferrari, F., Paris, C., Maigret, B., Bidouil, C., Delaunay, S., Humeau, C., Chevalot, I. Journal of Molecular Catalysis B: Enzymatic, 101, 122-132 (2014).

2017



Intensification of anaerobic digestion process of agricultural and industrial wastes by injection of industrial H₂

Aline Lebranchu (3rd year)

Eric Olmos and Michel Fick

Axe 3 | BioProMo



Keywords: Anaerobic digestion, Biological methanation, Hydrogen, Rheology, Gas/liquid mass transfer

General context, scientific issues

Anaerobic digestion process needs further development to enhance its economical profitability. Indeed, a biogas plant typically produces a mixture of CH₄ (60%) and CO₂ (40 %), suggesting a possible increase in CH₄ content in biogas. One way of improvement consists in injecting H₂ in the digester as some archaeobacteria consume H₂ and CO₂ to product CH₄. This biological reaction is called bi-methanation.

Objectives and stakes

The goal of this study is to increase the proportion of CH₄ in the biogas. To reach it, we had to answer to these questions:

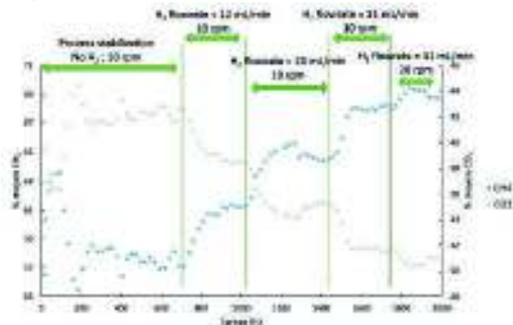
- Which design for the bioreactor?
- Which technology for H₂ injection?
- Is H₂ injection efficient to enhance the CH₄ content in biogas produced in a 100 L digester?

Methodology / Experimental approach

The first difficulty is that cattle manure is *a priori* a viscous shear-thinning fluid, raising key issues of bioreactor homogenization. As helical ribbons are reputed efficient for non-newtonian homogenization, a dedicated vessel equipped with a double helical ribbon was designed and built. Rheological characterizations of grinded cattle manure and digestate were first performed. Using the determined rheological law, a CFD study has been made to numerically simulate the hydrodynamic profile of the digestate in a reactor equipped with a helical ribbon.

The second step of this project was dedicated to gas-liquid mass transfer optimization. In order to avoid the release of H₂ in atmosphere, a bubble-free system was designed. This one consisted in a permeation system with a silicon membrane tubing. CFD simulations were made with this permeation tube to evaluate the H₂ dispersion in the reactor for different configurations of tubing. Finally, a 100 L pilot equipped with the helical ribbon and the best permeation configuration was designed and built to conduct biomethanation experiments. Various conditions of H₂ flowrates and agitation frequencies have been studied.

Illustration: Impact of H₂ injection on biogas composition



Main results

CFD studies showed:

- An efficient mixing in cattle manure with a helical ribbon.
- An efficient H₂ distribution with a cylindrical support of tubing with large diameter and addition of a screw-stirrer placed on the axis of the first ribbon.

H₂ injection has been made, in the 100-L pilot, in different conditions of H₂ flowrate (12, 20, 31 mL/min) and agitation frequencies (10, 20 rpm). The H₂-injection led to an increase in CH₄ content in the biogas and a decrease in CO₂ content.

At 10 rpm: 57, 61, 64 and 68 % have been obtained in CH₄ content respectively before injection, at 0, 12, 20 and 31 mL/min. The decrease in CO₂ content was from 43 %, initially, to 39, 35 and 31 % in the same conditions, as previously described.

Only traces of H₂ were detected in the biogas (between 0.01 and 0.03 %). This confirmed the efficient transfer and consumption of H₂ in relationships with the increase in CH₄ content in the biogas.

The increase from 10 to 20 rpm led to an additional increase in CH₄ content, corresponding to a better H₂ transfer in the manure. Up to 69.5 % CH₄ were reached.

References

Lebranchu, A.; Blanchard, F.; Delaunay, S.; Pacaud, S.; Marchal, P.; Fick, M.; Olmos, E. Utilisation de mesures de viscosités pour le calcul du mélange dans un digesteur. Journées Recherches et Innovation, (Avril 2014), Beauvais

2017 	<i>In-situ</i> identification and quantification of functional parameters of animal cells cultured in bioreactor by using spectroscopic tools <u>Li Mengyao (2nd year)</u> Annie Marc, Bruno Ebel Axe 3 BioProcesses-BioMolecules	
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Keywords: Bioprocess; Mammalian cell culture; Recombinant monoclonal antibody; Glycosylation; *In situ* spectroscopies (Dielectric, NIR, Raman); Chemometrics; Process control

General context, scientific issues
 Bioprocesses of mammalian cell culture have become essential for the production of therapeutic recombinant proteins. Consequently, it is important to control the production process and ensure the quality and the safety of end-products by using the PAT (Process Analytical Technology) approach initiated by the FDA. In this context, spectroscopic technologies combined with chemometric methods have gained great attention over the past decade as *in-situ* tools to monitor and control bioprocesses in real time.

Objectives and stakes
 Development of *in-situ* monitoring of functional parameters of CHO cells producing therapeutic monoclonal antibody (mAb) cultured in bioreactors:

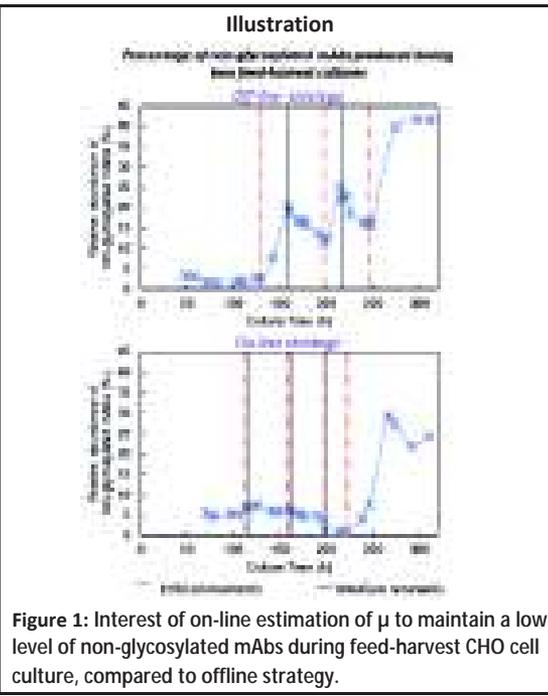
- Use of spectroscopic sensors implemented in bioreactors and development of real time spectroscopic models to predict, not only the concentration of different analytes, but also the kinetic parameters and the quality of the mAb produced.
- Implementation of on-line spectroscopic models to different cell culture bioprocesses (batch, fed-batch, feed-harvest, perfused), in order to have a better understanding of the culture process and a good control of the product quality.

Methodology / Experimental approach
Bioreactor cell culture experiments

- *In-situ* experimental data acquisition by conventional sensors (pH, temperature, dissolved O₂) and spectroscopic sensors (di-electric, Near InfraRed, Raman).
- Off-line characterization of cell populations (viable, dead, lysed cells), medium composition (glucose, lactate, glutamine, ammonium, LDH), and mAb (glycosylation), using HPLC, LCMS/MS, enzymatic methods...

Development / implementation of prediction models

- Model calibration by combining off-line measurements with on-line spectral data using PLS regression methods.
- Model optimization by comparison and combination of different types of spectroscopic data.
- Process control based on *in-situ* spectroscopies to achieve better culture performance and product quality.



Main results

- On-line prediction models have been developed using *in-situ* NIR and Raman spectroscopies, to monitor different culture parameters (concentration of viable cells, glucose, lactate, glutamine, ammonium, mAb). The model performances of both spectroscopies have been compared.
- For the first time, one of the most important mAb quality attributes, the glycosylation, was successfully monitored *in-situ* and in real time by Raman spectroscopy.
- A novel method of on-line estimation of cell specific growth rate (μ) was developed using dielectric spectroscopy. Implementation of the method in feed-harvest cultures has maintained a low level of non-glycosylated mAb (Fig. 1).

References

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 [2] Li M, Ebel B, Fournier F, Guedon E, Marc A, ESACT meeting (2017)

<p>2017</p> 	<p>Characterization and physiological impact of the hydrodynamics on expansion of human mesenchymal stem cells in bioreactors</p> <p><u>Céline LOUBIERE (2nd year)</u></p> <p>Eric OLMOS, Emmanuel GUEDON</p> <p>Axe 3 BioProMo</p>	
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Keywords: human mesenchymal stem cells, bioreactor, expansion process, hydrodynamics, microcarriers, CFD.

General context, scientific issues

Mesenchymal Stem Cells (MSC) show great interest for medical purposes: tissue engineering (bone, cartilage, tendon...) and cell therapy (heart diseases, cancer, auto immune diseases...). In order to reach a large scale production, which is required to obtain the high cell dose requirements, it is necessary to optimize the expansion process in 3D culture systems and especially the hydromechanical stress generated in the vessel. Because these cells need an adherence surface to proliferate, spherical solid particles, called microcarriers, are used and set in suspension in stirred tank bioreactors.

With the aim of improving the process, while maintaining the initial stem cell quality and the differentiation capacities, the impacts of the hydrodynamics on expansion yields are studied.

Objectives and stakes

- ▶ Determination of the hydrodynamics encountered in culture bioreactors by CFD and experimental approaches (hydromechanical stress, turbulent kinetic energy dissipation, microcarriers collisions and spatial distributions).
- ▶ Impact of characterized mixing conditions on MSC expansion yield and cell quality.
- ▶ Design of an innovative culture bioreactor and scale up till a few liter working volume.

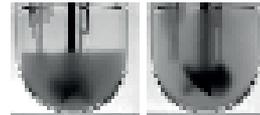
Methodology / Experimental approach

- ▶ Validation of static and dynamic expansion cultures protocols of human Umbilical Cord MSC in a culture medium supplemented with human platelet lysates and investigation of an optimized microcarrier between 6 commercial ones.
- ▶ Development of an empirical monomial correlation based on a design of experiments of 90 N_{js} measurements varying geometric parameters (type, size and off-bottom clearance of the impeller) and the type of microcarrier (diameter and density) and dimensional analysis of these different parameters impact on N_{js} value.
- ▶ Establishment of a CFD-based method to predict N_{js} and hydromechanical stress in the reactor (MRF Euler-Euler granular approach, k- ϵ turbulence model with adapted drag and turbulent dispersion force models)
- ▶ Impact of characterized hydrodynamics on cell proliferation yields and cell quality.

Illustration:



Human Umbilical Cord MSC adhered on microcarriers.



Microcarriers in suspension at $N = N_{js}$ for two impellers designs (EE up-pumping et EE down-pumping) in a bioreactor.

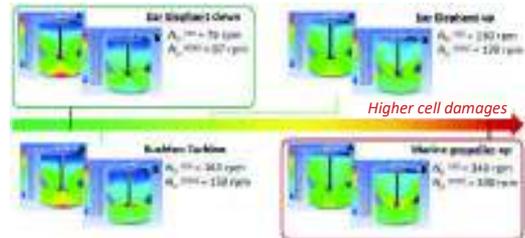
Main results

- ▶ Human Umbilical Cord MSC culture was validated in medium supplemented with human platelet lysates, and with adapted protocols for static and dynamic conditions and revealed better yields than with Bone Marrow MSC cultures.
- ▶ An empirical monomial correlation has been established to predict N_{js} with a mean error of 9,5 %.



Comparison of experimental and modeled N_{js}

- ▶ Application of the CFD-based method in mini scale bioreactors showed that the EE down-pumping impeller led to lower hydromechanical stress.



Microcarrier volume fractions (a) and turbulent dissipation rate (B) distributions in mini-bioreactors

References

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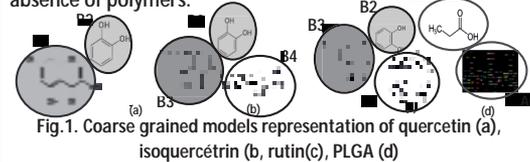
2017 	Development of a multi-scale approach to study interactions between flavonoids and biopolymers in different media <u>Manel SLIMANE (4rd year)</u> Mohamed GHOUL, Latifa CHEBIL Axe 3 BioProMo	
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Keywords: Flavonoids; solvent; biopolymers; multiscale approach; molecular modeling; mesoscale modeling; Dissipative particle dynamics; MesoDyn.

General context, scientific issues
 Polyphenols constitute an important class of bioactive molecules [1]. Flavonoids, as the most known polyphenols, are particularly promising candidates for use as functional foods and novel therapeutics due to their prominent biological activities. Some flavonoids have high antioxidant capacity, which has been shown to be higher than those of vitamins E and C in vitro studies. But, the major barriers to flavonoid use in different formulations are their poor solubility and low stability in common solvents, which consequently results in poor activity [2].

Objectives and stakes
 The objective of this thesis is to identify the main groups implicated in the solubility and the dispersion of flavonoids in presence of biopolymers in several media. In order to achieve this objective a double approach, experimental and modeling, was carried out.

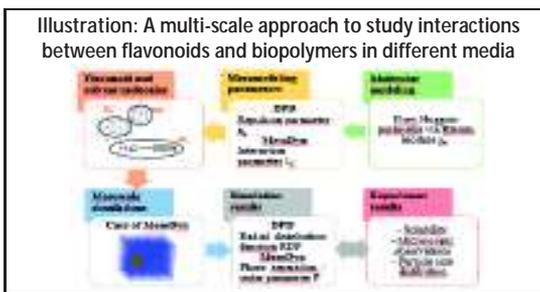
Methodology / Experimental approach
 1. Modeling approach: The different systems composed by flavonoids (quercetin "Q", rutin "R" and isoquercitrin "I"), solvents (acetonitrile "AC" and tert-amyl alcohol "MB") and poly (lactic-co-glycolic acid "PLGA") were represented as a coarse grained models. Molecular and mesoscale modeling tools will be used to identify processes that control both the solubility and the stability of flavonoids in different solvents in presence and in absence of polymers.



1.1. Molecular modeling: Input parameters: Method (Monte-Carlo); Module (Blends in Material studio 7.0); Forcefield (CompassII); temperature (50°C)/ Output parameters (Flory Huggins parameters χ_{ij}) / molecular dynamics: solubility parameter via molecular dynamics.

1.2. Mesoscale modeling: DPD input parameters: repulsion parameters (a_{ij}); system size (210*210*210 Å); total simulation time (25 10⁴ ps); temperature (50 °C). DPD output parameter (Radial distribution function analysis RDF). Mesodyn input parameters: interaction parameters (λ_{ij}); grid size (32*32*32); total simulation time (5 10⁴ μs); temperature (50 °C). Mesodyn output parameters: phase separation; order parameter.

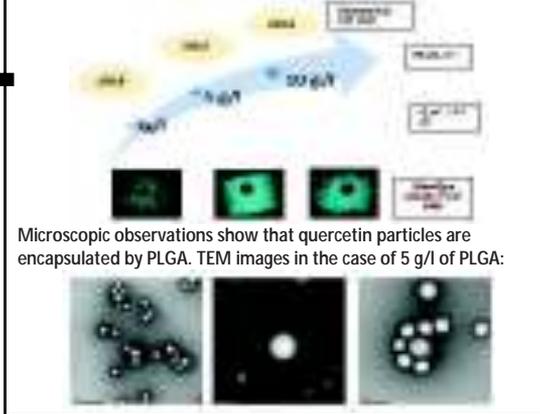
2. Experimental approach: solubility (HPLC); nanoprecipitation, agglomeration behavior.



Main results
 1. Study of solubility
 From molecular and mesoscale modeling some information were deduced:
 - B2 group (similar in the three flavonoids) have favorable interactions with MB deduced from small χ_{ij} values. Thus, it is responsible for the high solubility of quercetin, isoquercitrin and rutin in MB. Those results are in accordance with experimental founds. Solubility values in g/L.

Flavonoid	MB	AC
Q	0.70	0.10
R	0.65	0.15
I	0.60	0.20

2. Encapsulation
 Experimental, molecular dynamics and mesoscale simulations were done to elucidate the behavior of quercetin within PLGA (encapsulation). By varying PLGA concentration from 1 to 10 g/l, those results were obtained:



References
 [1] (Malbert et Al, 2014)
 [2] (Gao et Al, 2008)
 [3] (Chebil et Al, 2013)

<p>2017</p> 	<p>TiO₂ nanoparticles coupled to photosensitizers for applications in photocatalysis and photodynamic therapy</p> <p>Zahraa YOUSSEF (3rd year)</p> <p>Thibault ROQUES-CARMES – Céline FROCHOT</p> <p>Axe 3 BioProMo</p>	
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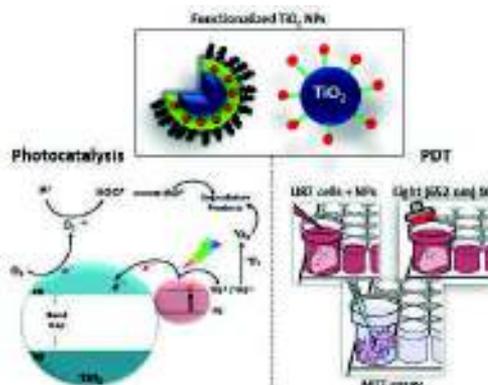
Keywords: Titanium dioxide, photosensitizer, covalent coupling, photocatalysis, photodynamic therapy

General context, scientific issues

Photocatalysis, which is a 'green' technology used for the purification and treatment of polluted water, has gained much attention [1]. In parallel, the fight against malignant cancer cells through photodynamic therapy (PDT) has always been challenging for researchers [2]. Owing to its non-toxicity, superior photoreactivity, photostability, high oxidizing capability and unique phototoxic effect upon irradiation, titanium dioxide nanoparticles (TiO₂ NPs) has been extensively long-used in photocatalysis and more recently employed in PDT [3]. In those applications, TiO₂ suffers from its large band gap energy, UV-limited photoresponse and fast recombination rate of the photogenerated electron-hole pairs.

Developing a titania-based system with a prolonged photo-response may overcome those limitations.

Illustration:



Objectives and stakes

In the present study, titania NPs are functionalized by visible light sensitive organic photosensitizer (PS) molecules namely Chlorin e6 (Ce6) and monocarboxylic tetraphenyl porphyrin (P1-COOH).

Prior to sensitization with PS, TiO₂ P25 NPs are modified through silanization *via* two different approaches. Such nanosystems would enable the production of different reactive oxygen species (ROS) capable of augmenting the NPs' efficiencies in PDT and photocatalysis.

Main results

Hybridized titania-based NPs silanized via two different approaches and coupled to a PS (Ce6, P1-COOH) are synthesized and characterized. The UV-visible Absorption profile of TiO₂ is extended to visible in both nanosystems and the PS is grafted covalently *via* amide bond. The modified NPs exhibit fluorescence and produce singlet oxygen.



Photocatalysis against methyl orange (MO): TiO₂-APTES-PS NPs possess a superior photocatalytic activity over the core-shell nanosystem under solar light and also over bare TiO₂ under visible light. T-A-Ce6 exhibits the best photocatalytic activity among all especially under pure visible light (80% of MO degraded after 120 min of irradiation).



PDT: Unlike core-shell NPs, T-A-Ce6 nanosystem appears to induce a relevant phototoxicity upon illumination at 10 J/cm² (652 nm). When illuminated, the cell viability decreased to reach 11% in the presence of T-A-Ce6 at 200 µg/mL corresponding to 0.22 µM of Ce6. The same photodynamic effect can be achieved with free Ce6 but using a higher concentration of 10 µM.

In T-A-Ce6 NPs, under visible light, Ce6 produces ¹O₂ and induces the indirect excitation of TiO₂ through electron transfer generating HO[•].

Methodology/ Experimental approach

The synthesis of functionalized TiO₂ NPs via 2 approaches:

1. Core-Shell nanosystem: In DEG, TiO₂ P25 core is encapsulated within a polysiloxane layer formed by the condensation/polymerization of APTES and TEOS silanes. The activated PS (P1-COOH, Ce6) is grafted *via* an amide covalent bond onto the shell. Finally, hydrophilic PEG is grafted onto the surface of the hybrid NPs.
2. APTES-modified nanosystem: TiO₂ P25 NPs are only silanized by APTES which is employed as a bridging molecule to covalently link the grafted PS (P1-COOH, Ce6).

Both nanosystems are characterized by: UV-Visible spectroscopy, zeta potential, DLS, FTIR, fluorescence spectroscopy, TEM, XRD... ROS (¹O₂, HO[•]) generation

Application:

1. Photocatalysis: The photodegradation efficiency of the NPs towards model pollutants (ex: methyl orange) is studied
2. PDT: anti-cancer capability of those NPs was assessed through *in vitro* experiments using U87 glioblastoma cell line exposed to different concentrations of NPs

References

- [1] Lü et al., Spectrochimica Acta Part A, 2013, p. 111:161-168
- [2] Bechet et al., Trends in biotech., 2008, p. 612-621
- [3] Huana et al., Catalysis Communications, 2009, p. 58-61

2017	Application of <i>in situ</i> near-infrared spectroscopy (NIRS) for monitoring biopharmaceuticals production by cell cultures	
	<u>ZAVALA Daniel (1st year)</u> Emmanuel GUEDON, Bruno EBEL Axe 3 BioProMo	

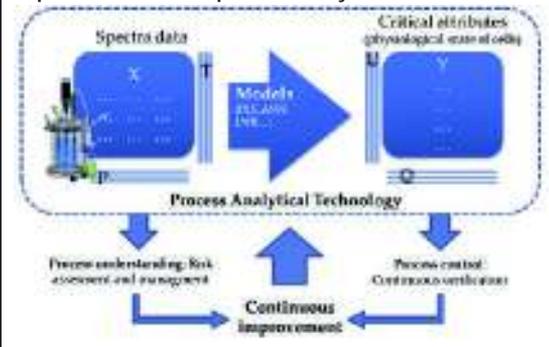
Keywords: Chemometrics, mammalian cell culture, plant cell culture, recombinant monoclonal antibody, Process Analytical Technology-PAT.

General context, scientific issues
Cell culture technology is nowadays the main and preferred method to produce large and complex molecules used as medicines to treat diseases such as immunologic diseases, cancer, heredity deficiencies, etc. In order to ensure quality and thus patient safety, optimal control of the production processes of these drugs is essential. In this context, several regulatory agencies have initiated the PAT approach to design, analyse and control the production process through real time measurements of critical quality attributes of in-process materials with the goal of ensuring final product quality consistency¹. Despite of cell culture technology progress, the analysis of physiological state of cells in biopharmaceutical bioprocesses remains mainly performed by *off-line* techniques, this could lead to delays adjustment of process perturbations². Spectroscopic techniques such as NIRS have gained relevance as PAT tool³, but there are still several challenges to overcome.

Objectives and stakes
Based on the quality by design-QbD paradigm, the main objective is to improve biopharmaceuticals production by cell cultures (plants and animal cells) with focus on monitoring and control of the process at bioreactor level using NIRS multiparametric calibration models.

Methodology / Experimental approach
Methodology is mainly based in three phases: 1) Generate plant cell lines; characterization and identification of critical parameters affecting biopharmaceuticals production by plant (*C. roseus*) and animal (CHO) cell cultures. 2) Performing cell cultures in bioreactors coupled to online NIRS measurements in order to obtain spectroscopic data. In association with measurement performed with conventional analytical methods, calibration models of critical parameters identified in phase one will be established. 3) Validation of chemometric models.

Illustration: Calibration models basis: benefits of their implementation into production cycle.



Main results
Four plant cell lines have been developed and partially characterised: specific light exposure and plant growth regulator regimen determines cell growth.

Until our knowledge, this work would be the first to undertake the PAT initiative through NIRS techniques in plant cell culture. This work would also provide innovative methods to monitor critical attributes during biopharmaceuticals (plant antineoplastics and mammalian antibodies) production by cell cultures. A remarkable aspect of the work is the focus on cell physiological state.

The construction of robust calibration models would eventually let them to be used in a variety of biopharmaceutical cell cultures.

References

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[2] Tamburini E., Marchetti M.G., Pedrini P. 2014. Monitoring Key Parameters in Bioprocesses Using Near-Infrared Technology. *Sensors (Basel, Switzerland)*. 14(10):18941-18959

[3] Næs T., Isaksson T., Fearn T., Davies T. 2004. A user friendly guide to Multivariate Calibration and Classification. NIR Publications, Chischester, U.K.



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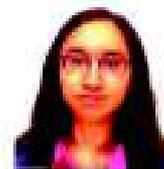
REACTIVITÉ
ET GÉNIE
DES PROCÉDÉS

2017

Preventive approach for a reduction of Polycyclic Aromatic Hydrocarbons (PAHs) in pyrolysis furnaces □ Application to low-pressure gas carburizing



Tsilla Bensabath (4th year)

Pierre-Alexandre Glaude, Hubert Monnier
Axe 4 | KinCom | INRSKeywords: PAHs; benzo[*a*]pyrene; low-pressure gas carburizing; acetylene pyrolysis; kinetic modeling

General context, scientific issues

Low-pressure gas carburizing is a heat treatment process used to harden surface of steel by enriching the metal with carbon atoms coming from pyrolysis of hydrocarbons. At the same time, reactions take place in the gas phase and lead to the formation of Polycyclic Aromatic Hydrocarbons (PAHs), precursors of soot. Released into the atmosphere or adsorbed on soot, PAHs are toxic to humans and hazardous to the environment. Some of them, such as benzo[*a*]pyrene (C₂₀H₁₂), are known carcinogens. Activities such as furnace maintenance and cleaning may thus represent a risk to workers.

Objectives and stakes

The objectives of the study are:

- to experimentally quantify products of acetylene (C₂H₂) pyrolysis and, especially, 16 PAHs classified as priority pollutants by the United States Environmental Protection Agency (US EPA);
- to produce a detailed kinetic model for light hydrocarbon pyrolysis describing reaction pathways leading to PAH formation.

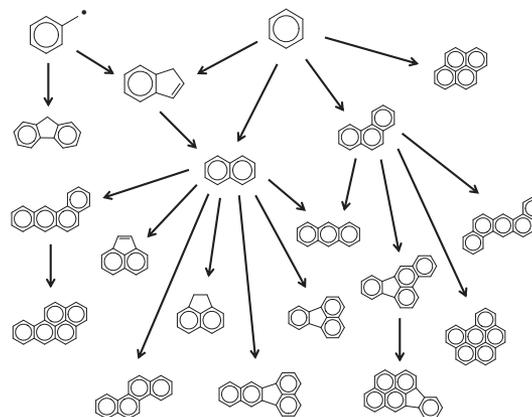
The aim is to understand the phenomena of PAH formation and growth in order to find operating conditions to make safer the low-pressure gas carburizing processes.

Methodology / Experimental approach

Experimentally, acetylene is pyrolysed at 900°C and 8 kPa into two reactors: a plug-flow and a CSTR, at different residence times (between 0.5 and 3 s) and reactant concentrations (20%, 50% or 100% in nitrogen). Light products are analyzed on-line by GC (TCD and FID detectors) and the 16 EPA-PAHs are recovered and analyzed off-line by GC-MS and HPLC (fluorescence detector).

The construction of the detailed kinetic model is based on a mechanism for the combustion of aromatic compounds. It was modified to adapt it to our conditions (pyrolysis, low pressure, etc.), and completed to take into account heavy PAHs up to seven aromatic rings [1].

Illustration: Growth of PAHs from first aromatic rings during acetylene pyrolysis



Main results

Experimental results show that acetylene conversion increases with reactant concentration at the inlet of the reactor and with residence time. At low concentration, the fraction of PAHs increases with residence time. It decreases with pure acetylene.

The model well describes the consumption of acetylene and the formation of light products. It reproduces reasonably well the orders of magnitude for PAHs.

The model was used to realize flux analysis in order to determine the main reaction pathways. The role of vinylacetylene and of benzene during acetylene pyrolysis is highlighted. The HACA mechanism (Hydrogen Abstraction C₂H₂ Addition) and the additions of aromatic radicals on aromatic molecules are the most important pathways for PAH growth.

Comparisons between reactants (acetylene, ethylene, propane) were also realized and the influence of pressure was tested with the model. It appears that the residence time impacts on the hydrocarbon which produces most PAHs. The production of PAHs increases with pressure.

Reference

[1] T. Bensabath, H. Monnier, P.-A. Glaude, *Journal of Analytical and Applied Pyrolysis* 122 (2016) 342-354

2017 	PhD subject : Purification of bio-oils from lignin liquefaction to produce high valuable molecules <u>Laëtitia Cesari (3rd year)</u> Fabrice Mutelet, Laetitia Canabady-Rochelle Axe 4 ThermE	
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Keywords: Bio-oils, phenols, ionic liquid, phase equilibria, process design, antioxidant properties, ab initio calculations (Gaussian 90), gas chromatography (GC), FID, TCD, mass spectroscopy (MS), UV-spectroscopy

General context, scientific issues

With their antioxidant properties, phenolic compounds can be used as first raw material in perfumery, food additive or drug industry. Nowadays, phenolic compounds are mainly produced from petroleum industry. Yet, because of the rise of global warming and the depletion of fossil fuels, there is a primary need to find a new way of production for these compounds.[1]

Illustration: Bio-oil fractions extracted with ionic liquid



Objectives and stakes

The thermochemical conversion of lignin produces bio-oils, rich in phenolic compounds, whose extraction and purification still remain tough. Several methods, such as distillation, are not well adapted. Liquid-liquid extraction (LLE) with solvent is commonly used, despite some practical issues such as the distribution of phenolic compounds into the two phases. Interaction phenomena between solute and solvent play a major part in the LLE processes and can be studied at molecular scale with ab initio calculations.

The main goal of this PhD is to optimize phenolic compounds extraction for their antioxidant properties from bio-oils, from thermodynamic data and theoretical calculation.

Main results

- For all the phenolic compounds, it was observed that each optimal conformation presents the hydroxyl group in the plan of the benzene ring. Vanillin, guaiacol, syringol and pyrocatechol are also more stable in the presence of intramolecular hydrogen bond. Moreover, comparisons of the rotational potential functions of the molecule highlights the presence of pattern proper to each substituent and their neighbours. In the presence of water, phenol, cresols and pyrocatechol adopt a translinear conformation whereas guaiacol and syringol present a cyclic one.

- The study of phase equilibria allowed the regression of the NRTL and UNIQUAC thermodynamic model parameters. Therefore, we design a process containing one multi-step extraction column and a flash. This process using ionic liquid as a solvent is simpler and economically competitive towards other "organic processes".[2]

- Extraction of phenolic compounds from bio-oils are more effective with ionic liquid. For instance, only one step is enough to extract more than 90% of phenol.

- All phenolic compounds present a radical scavenging capacity. Moreover, all phenolic compounds are high reducers, especially pyrocatechol, guaiacol and syringol. Guaiacol is also the most reactive molecule with the Folin-Ciocalteu's test. Finally, all the studied compounds have difficulties to chelate transition metals. Only pyrocatechol and vanillin show a low chelation power.

Methodology / Experimental approach

The study was led by a multi-scale approach:

- Ab initio calculation allowed the understanding of interaction phenomena at micromolecular scale. Molecules were studied in their isolated forms with a high level of theory and a high basis set. Then, a water molecule addition allowed the determination of the modifications at a structural scale.

- At macroscopic scale, the behaviour of phenolic compounds was studied in contact with several solvent (water, ethanol, ionic liquid). Phase equilibria were experimentally analysed for eight model molecules in binary and ternary systems.

- Extractions were performed on real bio-oils using different solvents. GC quantification the phases allowed the comparison of extraction efficiency for each studied solvent.

- Finally, antioxidant properties of model molecules were investigated by UV-spectroscopy.

References

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 [2]L. Cesari, L. Canabady-Rochelle, F. Mutelet, Fluid Phase Equilibria. 446 (2017) 28–35. doi:10.1016/j.fluid.2017.04.022

2017	<p>Detailed chemical modeling of biomass combustion in domestic heating appliances in order to reduce their polluting emissions</p> <p>Amal DHAHAK (2nd year)</p> <p>LRGP: Frédérique BATTIN-LECLERC, Roda BOUNACEUR and Olivier HERBINET, CSTB: Céline LE DREFF, ADEME: Florence PROHARAM</p> <p>Axe CITERE GCR</p>	
<p>Keywords: Biomass, Combustion, Pyrolysis, Kinetics, Modelling, Emissions</p>		

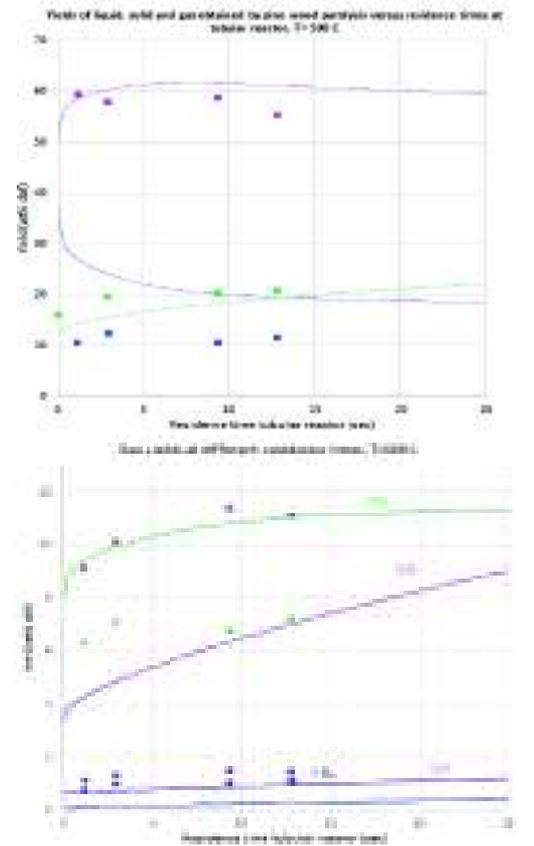
General context, scientific issues
The use of heating systems by burning biomass is expanding rapidly. Although these technologies offer many benefits, they are a significant source of gaseous pollutants that can have adverse effects on the environment and human health.

Objectives and stakes
This thesis aims to understand and model the chemical mechanisms of biomass combustion in domestic heating appliances in order to reduce polluting emissions. It includes an experimental part carried out during punctual test campaigns with the CSTB, and a modeling part carried out at the LRGP. This modeling part is the heart of this project; the experimental part is used to provide input data and to validate the developed model. The aim of this thesis is to develop a model that will couple a physical approach describing thermal transfer with a semi-detailed chemical model to reproduce the formation of pollutants in the gaseous phase. This chemical model will be based both on globalized reactions to simply represent the devolatilization of biomass and on detailed kinetic models to describe the evolution of species in the gaseous phase.

Methodology
The biomass is characterized as a mixture of three so-called reference constituents: cellulose, hemicellulose and lignin. The decomposition of biomass is therefore the combination of the pyrolysis of these three compounds [2]. Each biomass compound is represented by a reference species. Cellulose (CELL) is represented by the monomer (C₆H₁₀O₅). Xylan (C₅H₈O₄) is the monomer chosen for hemicellulose (HCELL). Lignin, having a complex structure, is represented by three reference compounds LIGC, LIGH, and LIGO (richer in C, H and O, respectively). The decomposition of wood is therefore the superposition of degradation of its compounds. It gives a large number of liquid, gas and solid species. These compounds will undergo secondary reactions to give rise to other species.




Illustration: Simulation performed during this study [2]



Main results
We have developed a database of different models used in the literature, as well as of experimental studies on pyrolysis and wood combustion. Then, we have conducted the benchmark of the selected model (RANZI)[1], as shown in the above illustration. The next step in progress, is to develop a more reliable model.

[1] E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, and S. Sommariva, "Chemical kinetics of biomass pyrolysis," *Energy and Fuels*, vol. 22, no. 6, pp. 4292–4300, 2008.
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2017 	Upgrading of thermoplastics waste by thermal process: experimental study and kinetic modelling <u>Asma DHAHAK (1st year)</u> Valerie BURKLE-VITZHUM, Guillaïn MAUVIEL Axe 4 GCR/GREENER	
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Keywords: kinetic modelling, thermal process, polymer materials, experimentation, thermoplastics

General context, scientific issues
 Pyrolysis is an endothermic reaction under an atmosphere free of oxygen. This method makes it possible to convert solid waste into useful products in different states (liquid, solid and gas). In our work, we choose firstly the polyethylene terephthalate (PET) which is a thermoplastic. It is mainly used in bottles, flasks, textiles.... Its chemical structure is in fig 1.



FIG 1: The structure of PET.

Objectives and stakes

In order to better understand the reactions involved, to develop and optimize the processes, it is necessary to have a reliable kinetic model, constructed according to a non-empirical methodology - as is often the case - Taking into account phenomena as they occur at the molecular level, while introducing model reduction methods necessary in the case of macromolecules. The stakes of this thesis are:

- 1) Writing mechanistic kinetic models lumped with thermal reactions of macromolecules (PET in a first time, but a methodology that could be generalizable to other polymers).
- 2) Estimation of associated speed constants.
- 3) Validation by pyrolysis experiments allowing quantitative and qualitative monitoring of the degradation products of the polymers.

Methodology / Experimental approach

The different steps of the study are:

- 1/ Preparation of an exhaustive bibliographic study.
- 2/ Experiments were carried out, firstly in a reactor presented in fig 2 and in characterizing the products obtained.
- 3/ Construction of a semi-detailed kinetic model and simulation by Chemkin software. A possible mechanism of PET degradation is shown in fig 3 [1].



FIG 2: A scheme of experimental installation.

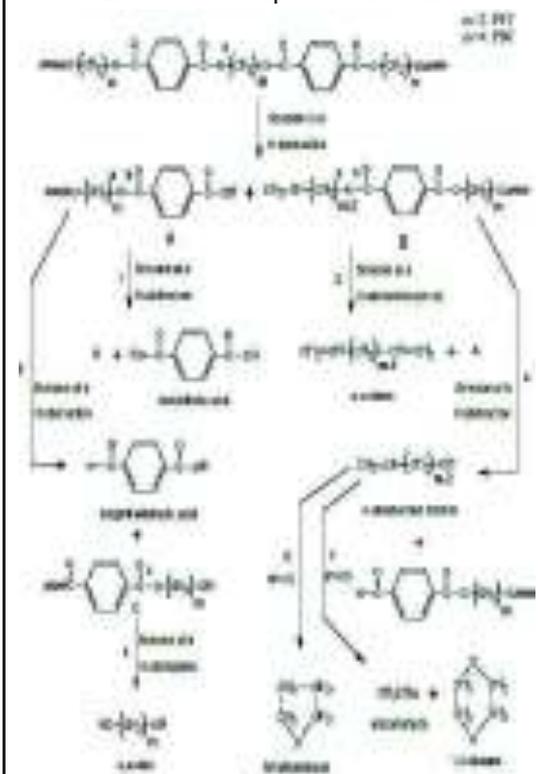


Fig 3: The thermal degradation Mechanism of PET by MC Neill [1].

References

[1] MC Neill, M. Bounekhel, « Thermal Degradation Studies of Terephthalate Polyesters: 1- Poly(alkylene terephthalate) », in Polymer Degradation and Stability, volume 34, 1991, pp. 187-204.



Keywords:

combustion kinetics, flame diagnostics, FAME, FAEE, laminar flame, premixed flame

General context, scientific issues

Global climate change concern has motivated interest to renewable energy sources that offer the potential of zero net CO₂ emissions. Declining worldwide supplies of conventional petroleum-based hydrocarbon fuels for industrial and transportation applications are also leading toward alternative fuel sources. One promising solution of these challenges is the use of fuels produced by biological systems that have a zero contribution to the CO₂ cycle in the atmosphere. Biodiesels are among the most viable liquid transportation fuels for the foreseeable future. Development of detailed chemical kinetic mechanisms for combustion of biodiesel components could significantly facilitate the prediction of combustion characteristics of such fuels, but the lack of experimental data on combustion chemistry of ester-based fuels in various conditions (pressure, mixing conditions etc.) makes the development of such mechanisms considerably difficult (if not impossible).

Objectives and stakes

Premixed stoichiometric and fuel-rich flames (fuel/O₂/Ar) stabilized on flat burners at low (50 Torr) and atmospheric pressure fueled with the following compounds are scheduled to be studied:

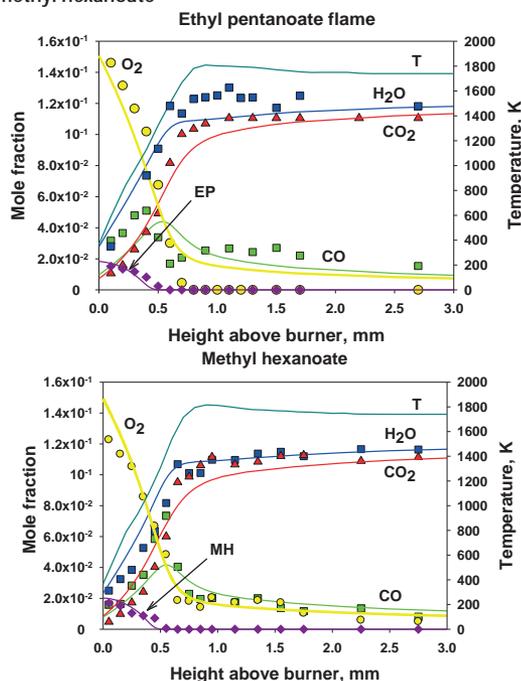
- Ethyl acetate and methyl propanoate
- Ethyl butanoate and methyl pentanoate
- Ethyl pentanoate and methyl hexanoate
- n-Heptane/ethyl pentanoate (this mixture represents a model of realistic hydrocarbon fuel mixed with ethyl ester-based biodiesel)

Methodology / Experimental approach

• Gas chromatography (GC) at low-pressure conditions (LRGP, Nancy) [1]; this technique permits a quantification of the stable products and an easy separation of the isomers. A thin probe, which induces less thermal and flow perturbation in the flame, will be used.

• Molecular-beam mass-spectrometry (MBMS) with soft ionization by electron impact at atmospheric pressure (ICKC, Novosibirsk) [2]; this technique permits to measure mole fraction profiles of unstable products due to a sonic probe.

Illustration: Mole fraction profiles of major species and temperature profiles in the flames of ethyl pentanoate and methyl hexanoate



Main results

Spatial distribution of reagents, main products and intermediates in flames were measured at atmospheric pressure. Temperature profiles were measured too. A comparison between experimental results and modeling data (using mechanisms [3] and [4]) was performed to check out the main discrepancies. Kinetic analysis was also performed.

Future work aims to measure mole fraction profiles of main components and intermediates in the above-mentioned flames at 50 Torr using GC and to upgrade the mechanisms according to new experimental data.

References

- [1] L.S. Tran, B. Sirjean, P.A. Glaude, K. Kohse-Höinghaus, F. Battin-Leclerc, Proc. Combust. Inst., 35 (2015), 1735-1743
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- [3] G. Dayma, C. Togbé, P. Dagaut, CM0901 3rd Annual Meeting, General Meeting in Nancy, 2011.
- [4] O.P. Korobeinichev, I.E. Gerasimov, D.A. Knyazkov, A.G. Shmakov, T.A. Bolshova, N. Hansen, C.K. Westbrook, G. Dayma,

<p>2017</p> 	<p>Research subject: Valorization of biomass and wastes by pyrolysis and gasification: optimization of the process efficiency, characterization of the various products and development of gas cleaning processes.</p> <p><u>Maxime Hervy (Ingénieur de recherche)</u></p> <p>Guillain Mauviel, Anthony Dufour Axe 4 GREENER</p>	
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Keywords: Biomass and waste valorization; Refuse Derived Fuel; Pyrolysis; Gasification; Syngas cleaning; Tar cracking; Heterogeneous catalysis; Thermal cracking; Hot filtration; Characterization of char, gas, tar and soot.

General context, scientific issues

To cope with the depletion of fossil fuel resources, the increase of waste generation and of the world energy demand, the pyro-gasification process appears as a promising solution. The pyro-gasification consists of the decomposition of a solid fuel in three phases: syngas, tars (organic pollutants), and a solid residue named char and/or ash. The syngas can be used in many applications depending on its purity.

The main issues for the development of pyro-gasification processes are: (i) to identify correlations between fuel composition - optimum gasification efficiency - pollutants production, and (ii) to develop efficient gas cleaning technologies.

Objectives and stakes

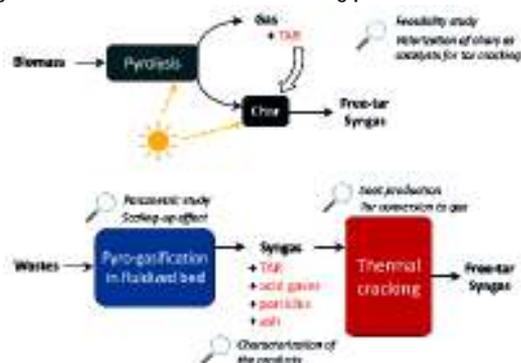
The three projects in which I am involved are focused on: (i) the optimization of refuse derived fuel gasification in fluidized bed, (ii) the development of analytical tools aiming at characterizing gaseous products, particulate matter (soot) and tar, (iii) the design of a thermal cracking process used to convert tar into permanent gases, (iv) the valorization of pyrolysis chars (solid residues) as catalysts for tar cracking reactions in a solar furnace device.

Methodology / Experimental approach

(1) To optimize the gasification efficiency of various wastes (refuse derived fuels) in a fluidized bed reactor, a parametric study will be realized in order to determine the relationships between the physico-chemical properties of the wastes (granulometry, chemical composition), the operating conditions (T, ER) and the process efficiency. A complete characterization of the products (ash, particulate matter, gaseous products, tar) is expected to improve the understanding of the mechanisms responsible for the pollutants production during the gasification process. The scaling-up effect will be studied by transferring the optimized conditions determined at lab-scale (5 kg/h of combustible) to pilot-scale (50 kg/h). This project named "TERRACOTTA" involves industrial (EDF, TIRU, EQTEC) and academic (LERMAB, LRGP) partners.

(2) To improve the understanding of the gasification -

Illustration: Scheme of the solar pyrolysis, waste gasification and tar thermal cracking processes.



- mechanisms, a complete characterization of the products is requested. In addition to gas, tar and char analysis, a particular attention will be pay to the characterization of acid gases and particulate matter in order to address the lack of knowledge in this specific field.

(3) A new thermal cracking process will be developed in order to convert the tar contained in the syngas into permanent gases, using high temperatures (1100-1300 °C). These reactions can also generate carbon particles named soot. The main objectives are (i) to improve the understanding of the soot formation mechanisms during tar cracking reactions, and (ii) to determine the conditions leading to the conversion of tar into gas and avoiding/reducing the formation of soot. This project is part of the Labcom "ASTARTE" in which several teams of the LRGP are involved together with the company Leroux & Lotz Technologies.

(4) Another research project deals with a new concept of solar conversion of biomass producing gas and chars. While biomass is pyrolysed in the upper part of the reactor, the primary vapors (tar and gas) flow through a char bed heated at high temperature (1100-1200 °C) by concentrated solar radiation, resulting in the catalytic cracking of the tar. This concept would allow the *in-situ* upgrading of the gas and the valorization of the chars. First, a feasibility study is performed using an image furnace to simulate solar radiation.

<p>2017</p> 	<p>Accurate and reliable calculation of thermodynamic properties of air-components mixtures, CCS fluids and innovative working fluids for closed power cycles</p> <p><u>Silvia Lasala (Post-doc')</u></p> <p>Supervisor 1: Jean-Noël Jaubert, Supervisor 2: Romain Privat Axe 4 ThermE Air Liquide</p>	 
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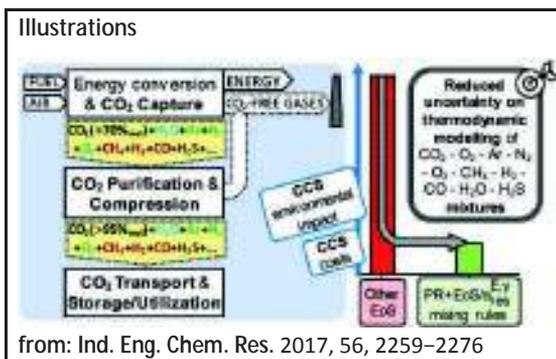
Keywords:
Thermodynamic models, air-component mixtures, CO₂ Capture and Storage (CCS) fluids, closed power cycles working fluids, working fluid design

General context

The main fields of research which I am working on focus on improving the understanding and modelling of the thermodynamics of fluids treated by two applications:

- cryogenic/refrigerated phase-separation processes for the purification of either air mixtures or fluids treated by CO₂-capture technologies;
- design of working fluids for closed power cycles.

These two main areas of research are developed in the context of the activities of the team ThermE of LRGP, which deal with the theoretical and experimental study of the thermodynamic properties of fluids for energy applications.



Targets, methodology and results

The first mentioned activity, about the “thermodynamics of fluids treated by cryogenic/refrigerated phase-separation processes”, has already brought the following results.

- The first part of my post-doctoral studies, funded by Air Liquide, has led to: (1) attest the superiority of GERG-2008 EoS in the calculation of air-components mixtures; (2) the development of a computational Fortran code based on GERG-2008 EoS, with a complete set of robust flash algorithms (PT, PH, PS, Pz, Tz, TH, TS, UV, SV, PV) and its coupling with Simulis Thermodynamics;
- My researches over the study of thermodynamic properties of fluids treated by CO₂-capture technologies began during my doctorate, partially developed in ThermE, which have led to the definition, optimization and application of an advanced and accurate equation of state for fluids treated by CO₂-capture processes, in particular composed of CO₂, N₂, Ar, O₂, CO, CH₄, H₂O, H₂S, H₂ (see Illustration).

Further developments

The second activity, about the “design of working fluids for closed power cycles”, is in the early stage of development and is part of a research project funded by ASME IGTI ORC Power Systems – Knowledge Center ORC, due to begin in October 2017.

This research aims at developing a computational program and an experimental set-up to enable the optimal design of mixtures by means of, respectively, reliable thermodynamic property calculations and thermal stability measurements of binary working fluids for closed thermodynamic cycles. Further preliminary researches on this work have led to include, among our targets, the design of reactive working fluids for closed power cycle applications.

Finally, it is highlighted that all these research activities are part of a more comprehensive long-term work undertaken by the team ThermE, aimed at developing a computer program being able to perform any thermodynamic calculation by means of a flexible code that implements the most robust algorithms and accurate thermodynamic models.

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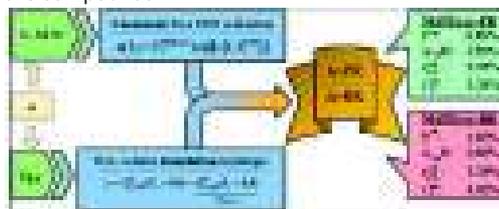
<p>2017</p> 	<p>Development of a cubic equation of state adapted to the representation of blends made of polar molecules (water, alcohol, amines...) and hydrocarbons</p> <p><u>Yohann Le Guennec (3rd year)</u></p> <p>Jean-Noël Jaubert, Romain Privat Axe 4 ThermE Funding by TOTAL</p>	
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Keywords: Phase equilibrium, cubic equations of state, pure compounds, mixing rules

General context, scientific issues

Thermodynamic models are widely used for the modelling and prediction of fluid phase behaviors in many different chemical engineering fields. Among the whole available models, cubic equations of state are preferred for their simplicity and accuracy. Therefore, highly efficient cubic equations of state able to represent more and more complex systems with increasing accuracy are always appreciated.

Illustration: *tc*-PR equation of state achievements for pure compounds



Objectives and stakes

The new cubic equation of state to be proposed should be able to represent pure compounds but also mixtures of variable complexity, including ideal and non-ideal systems and non-associated and associated systems. The selection of the optimal mixing rule for the thermodynamic model will be analyzed in details. Finally, a reference database of binary systems will be proposed for the validation of new thermodynamic models and will be freely available on the internet

Main results

The regression procedure of the α -function, simultaneously with the volume translation parameter with respect to the regressed experimental data has been extensively discussed and a general methodology has been proposed [1]. It was highlighted that any α -function should respect some mathematical criteria in order to (i) be extrapolated to the high-temperature and high-pressure domains and (ii) allow for a proper representation of binary mixtures [2-3]. The *tc*-PR model embeds such an α -function [4]. The *tc*-PR equation of state for pure compounds is very promising due to its excellent accuracy over both the thermodynamic and volume properties and will be extended to mixtures soon. A first step in this direction was achieved through the selection of a mixing rule for the volume translation parameter. It was demonstrated that only a linear one is acceptable [5].

Methodology / Experimental approach

Modelisation of pure compounds can be improved by modifying (i) the α -function and (ii) the volume translation parameter. A well-tuned α -function allows for accurate predictions of thermodynamic properties relevant for the sizing of processes such as the vapor pressure or the vaporization enthalpy. Still, a cubic equation of state with a good-enough α -function is unable to accurately estimate the density of a liquid phase. Thus, the volume translation method was proposed in the 80's with the benefit of significantly improving the density calculations while living unchanged the other, already well predicted, properties.

On the other hand, mixing rules embedded in the thermodynamic model must be studied to define which one allows for a better representation of the multicomponent systems. The new thermodynamic model, named *tc*-PR, with its own α -functions, volume translation parameters and mixing rules will be validated against experimental data issued from our newly proposed database.

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2017

Sulfur sequestration in Oil Reservoirs



Néstor Camilo LEGUIZAMÓN GUERRA (3rd year)

Valérie BURKLE-VITZTHUM, Raymond MICHELS
Axe 4 | GCR | GeoResources

Keywords: Free radical Kinetics, Organic Geochemistry, Petroleum, Sulfur, Pyrolysis, Gas Chromatography.

General context, scientific issues

To supply the growing energy demand associated to the increase in population and technological development, oil exploration has moved to unconventional sources like heavy oils found at high temperature and high pressure reservoirs, most of them associated with H₂S and sulfur compounds.

In order to make the exploitation of these oils cleaner and economically profitable, it is necessary to improve the current exploration tools based on the understanding of hydrocarbons geochemistry to guarantee the quality, phase and amount of the extractable resources.

After extraction and refining, Oil & Gas companies face the challenging treatment of H₂S and other acid gases. The re-injection into depleted oil and gas reservoirs has been proposed as a proper solution to this problem. The long term validation of this by-product management alternative requires a better knowledge of sulfured hydrocarbons geochemistry and kinetics to predict geological and chemical stability of the acid-gas-refilled reservoirs.

Objectives and stakes

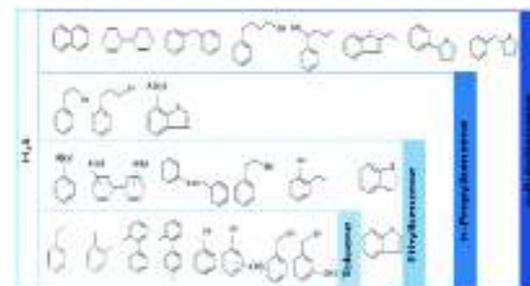
- Understanding the chemistry of sulfur in mixture with hydrocarbons in geological conditions and its effect on crude oil composition.
- Modelling hydrocarbons reactivity in sulfured oil reservoirs.
- Linking the reactivity prediction with the fluid migration into the reservoir formation.
- Completing and extrapolating the previous studies about oil pyrolysis under geological conditions including the role of H₂S.
- Envisaging the injection of H₂S into depleted oil reservoir as a strategy of environmental treatment of acid gases produced during extraction and refining of hydrocarbons.

Methodology / Experimental approach

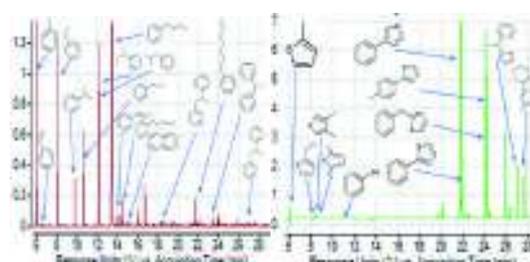
Confined pyrolysis under high pressure (700 bar) and temperature (310°C - 350°C): The sample mixture (alkylbenzene and H₂S) is introduced and sealed into a gold tube which is heated into an autoclave. The reaction time is set from 3 to 15 days and varies with the temperature to simulate the geological maturation age of the reservoir. The products are identified by GC-MS, quantified by vacuum thermal desorption coupled to a GC-FID and by a GC-FID-FPD system [1, 2].

Kinetic modelling: a detailed kinetic model is being constructed based on free-radical chemistry.

Illustration:



Main products of Alkylbenzene-H₂S pyrolysis (350°C, 700bar, 7 jours)



GC analysis of n-Butylbenzene-H₂S pyrolysis (350°C, 700bar, 15 jours).
GC-FID (red), GC-FPD (green).

Main results

Initial results of n-butyl benzene pyrolysis confirm the high stability of the aromatic cycle to thermal cracking.

Main reaction products of pure n-butyl benzene pyrolysis are shorter alkyl-benzenes (toluene, ethylbenzene and branched butyl benzene).

S-H bond whose energy is lower than the BDE of C-H promotes the formation of bi-aromatic sulfur compounds at high temperature pyrolysis. Low molecular weight sulfur compounds (Thiols, thiolanes and sulfures) decompose at pyrolysis conditions as intermediates in the formation of heavier sulfur compounds.

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2017	Prediction of thermokinetic parameters for liquid-phase oxidation from an equation of state based on the Statistical Associating Fluid Theory	
	<u>Edouard Moine (2nd year)</u> Romain Privat, Baptiste Sirjean, Jean-Noël Jaubert Axe 4 ThermE	

Keywords: Solvation, GIBBS energy of solvation, Perturbed-Chain SAFT equation of state, thermodynamics models, reaction mechanism, liquid-phase oxidation, kinetic constant

General context, scientific issues

Liquid-phase oxidation of hydrocarbons is an essential reaction for a large number of petrochemical processes. The simulation of this kind of reaction requires the use of detailed chemical kinetic models that contain thousands of species and reactions in liquid-phase. The estimation of accurate thermokinetic parameters in liquid phase is the main challenge for the development of liquid-phase kinetic models and requires new computational approaches.

Objectives and stakes

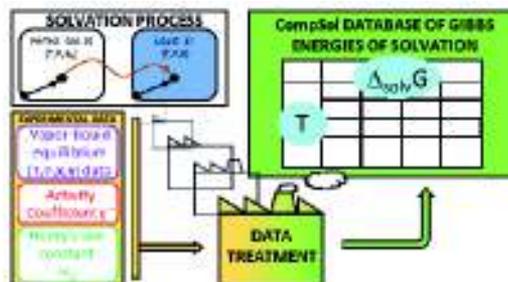
As these thermokinetic parameters can be easily estimated in gas phase using the Group Contribution concept, it is proposed to express liquid-phase parameters from gas-phase parameters by adding a correction term involving the so-called GIBBS energies of solvation of components. The main target of this thesis is to develop a robust PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory) equation of state (EoS) for the estimation of GIBBS energies of solvation, and then, to propose a novel tool for the generation of detailed kinetic models for liquid-phase oxidations.

Methodology / Experimental approach

This thesis is divided in three different steps:

1. Thanks to a thorough analysis of the solvation-process definition, direct links have been established between solvation energies and experimentally-accessible thermodynamic properties under certain temperature, pressure and composition conditions. A comprehensive databank of Gibbs energy, enthalpy and entropy of solvation for pure species and binary mixtures has been developed in the framework of this study.
2. The aforementioned databank will be used for the development of a well-parameterized SAFT-type equation of state devoted to the generation of Gibbs energy of solvation data. This work will make it possible to predict liquid phase thermokinetic constants of complex systems.
3. The tools developed for the prediction of thermokinetic constants in liquid-phase systems will be used to generate detailed kinetic mechanisms of liquid-phase oxidation processes.

Illustration: A methodology for the development of an extensive databank containing solvation energies



Main results

The developed databank (called *CompSol*) shows many advantages compared to other databanks of solvation energies:

- The number of pure-component solvation energy data was multiplied by 20.
- The number of binary systems was multiplied by 5.
- For each system, the *CompSol* databank contains Gibbs energy of solvation data at different temperatures.
- The *CompSol* databank contains also entropies and enthalpies of solvation.
- Based on all these experimental Gibbs energy of solvation data in binary mixtures, a link can be clearly highlighted between the solvation process (the fact that a solute will be well or poorly solvated by a solvent) and association phenomena (i.e., interaction between a solute and a solvent through hydrogen bonding).

Perspectives

- development of a SAFT-based equation of state capable of guesstimating Gibbs energies of solvation and activity coefficients as well.
- prediction of constant rates of complex systems in which liquid oxidation reactions take place.

References

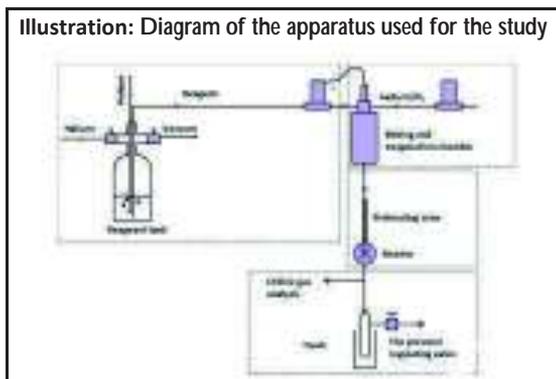
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<p>2017</p> 	<p>PhD subject : Experimental study of pollutants formation during the combustion of model molecules from bio-oil</p> <p><u>Sylvain Namysl (1st year)</u></p> <p>F. Battin-Leclerc, O. Herbinet Axe 4 GCR</p>	
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Keywords: bio-oil, pollutants, combustion, kinetic study, jet-stirred reactor

General context, scientific issues

In September 2016 the IMPROOF project started. This project is funded by the European Union and brings together 11 partners from 6 different countries, including the LRGP from Nancy. The aim is to improve the energy efficiency of steam cracking furnaces by an economical optimization and a reduction of pollutant emissions. For this purpose, laboratory studies and industrial pilots are carried out in order to improve the designs and materials of the furnaces. In parallel, modeling will be developed on these furnaces as well as the study of alternative fuels, especially those derived from biomass.



- Objectives and stakes**
- Determine a surrogate for bio-oil obtained by pyrolysis
 - Establish an experimental database to identify combustion products
 - Develop and validate detailed kinetic models in order to reproduce the combustion of the fuel

Main results

Experimental data obtained in this study showed differences in the reactivity of long chain alcohols and aldehydes. Many intermediates have been detected. These data have been used for the validation of detailed kinetic models developed by the partner Politecnico di Milano.

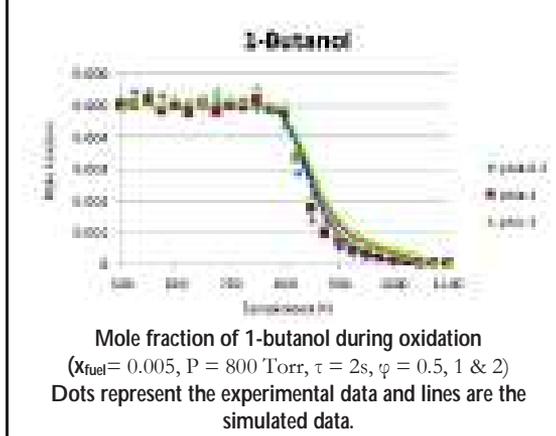
Methodology / Experimental approach

The composition of a bio-oil can be very variable considering some parameters. They are: biomass origin, pyrolysis temperature, age of the oil... A very large spectrum of molecules can therefore be found in the bio-oil, that's why a classification by functional group was made. The strategy consists in selecting model molecules which own the same functional group as molecules presents in the oil. Oxidation experiments were performed using a jet-stirred reactor. Thanks to its both homogeneity in temperature and concentration, it can be considered as an ideal reactor for kinetic studies.

Three gas chromatographs are used to detect a wide range of reaction products. Gas chromatograph are directly connected to the outlet of the reactor thanks a heated transfer line and injection valve (online analysis). They are used to quantify the products of reactions. A gas chromatograph coupled to a mass spectrometer is also used to identify the products.

Experiments were already carried on 1-pentanol, 1-butanol, butanal and pentanal. Next fuels will be butanoic acid and pentanoic acid.

It is also planned to study nitrogen containing fuels with special care taken to the formation of pollutants such as nitrogen oxides.



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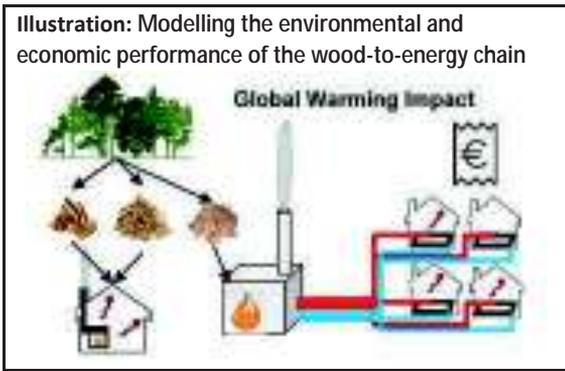
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<p>2016</p> 	<p>Environmental and socio-economic analysis of bioenergy production chains</p> <p><u>Chloé Pelletier (4th year)</u></p> <p>Anthony Dufour, Marie-Noëlle Pons, Patrice Dumas Axe 4 GREENER</p>	
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Keywords: biomass, modelling, Life Cycle Analysis, economics

General context, scientific issues

In order to achieve the European and French objectives for greenhouse gas (GHG) reduction and renewable energy increase, the share of energy produced from biomass is expected to rise greatly. France has large forests which are currently under-utilized and could be valorized energetically. However, wood can be converted using a number of different technologies. What are the environmental and economic advantages and drawbacks of each, on global as well as local scales?



Objectives and stakes

- Establish the Carbon, Oxygen, Hydrogen balance of the different production chains
- Do a Life Cycle Analysis and an economic analysis to compare the different scenarios

Main results

- In the Landes region, climate change projections result in a decrease in annual wood production as water stress episodes intensify.
- A first series of runs for combustion scenarios has shown that, for the production of heat, wood generally emits less GHG than natural gas or electricity, but is not always cheaper.
- The dynamic Life Cycle Analysis shows that the GWP of wood fuel increases with shorter forest rotation scenarios. The intensification of wood production is not an ideal response to the global warming issue.
- On the global scale, projections show that the competitiveness of wood for the production of energy depends strongly on the existence and level of carbon taxes. In the absence of such regulatory devices, wood is just too expensive compared to energy crops for example.

Methodology / Experimental approach

My thesis is part of the FORéVER project in which four laboratories collaborate.

The GO+ model, an ecophysiological growth model for forests, developed by INRA in Bordeaux, is coupled with CAT, a tool from LERFOB in Nancy that calculates the GHG emissions from the primary transformation of wood. This setup allows us to quantify the input and output from biomass growth and supply chain, over 50 to 100years, and under various climate change projections.

The resulting data feed process models for the different conversion scenarios (combustion and gasification). These models are developed under Aspen Plus© with Fortran subroutines for the more complex reactions. The combination of models and literature gives a complete Life Cycle Inventory, which is used for the environmental and economic analyses.

On the global scale, the competitiveness of wood with other sources of bioenergy is studied via the IMACLIM economic model (CIRED).

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<p>2017</p> 	<p>Post-doc subject : Experimental study of the formation of NO_x during the combustion of biogas</p> <p><u>Yu SONG (Post-doc)</u></p> <p>Supervisor 1 Frederique Battin-Leclerc, Supervisor 2 Olivier Herbinet Axe 4 GCR</p>	
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Keywords: biogas ; oxidation ; oscillation ; jet stirred reactor

General context, scientific issues

In September 2016 the IMPROOF project started. This project is funded by the European Union and brings together 11 partners from 6 different countries, including the LRGP from Nancy. The aim is to improve the energy efficiency of steam cracking furnaces by an economical optimization and a reduction of pollutant emissions. For this purpose, laboratory studies and industrial pilots are carried out in order to improve the designs and materials of the furnaces. In parallel, modelling will be developed on these furnaces as well as the study of alternative fuels, especially those derived from biomass.

Objectives and stakes

To investigate the influence of the addition of NO on combustion of biogas surrogates in an O₂/inert gas mixture at moderate temperatures in the quartz jet-stirred reactor.

To study the formation of NO_x during the biogas combustion performed at high temperatures using a newly designed flow reactor which will be built on purpose for this project. This reactor will be composed of a small ceramic tube included in a high temperature laboratory tubular furnace allowing reaching a maximum temperature up to 2000 K.

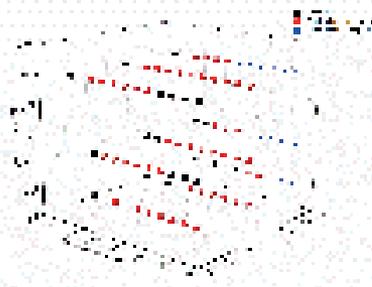
Methodology / Experimental approach

The measurements were performed in a jet-stirred reactor. The jet-stirred reactor used in this paper was designed following the rules established by the Villermaux team in the 70s. Its main advantage is that it can be easily modeled as a 0 dimensional ideal perfectly stirred reactor as the temperature and the composition in the reactor are homogenous. The experiments were carried out at a constant pressure of 1.06 bar, at a fixed residence time of 2 s, with temperatures ranging from 950 to 1200 K. The bath gas is carbon dioxide in this work.

Gas flow rates were controlled by mass flow controller. Oxygen and helium were provided by Messer and their purities are reported as 99.995% and 99.999%, respectively.

In order to measure the temperature inside the JSR reactor, a Pt13%Rh thermocouple which was marked at the silica-coated surface to ensure how further it is inside the reactor was inserted from the outlet of the reactor

Illustration: Temperature oscillation maps with various methane mole fraction (0.01-0.05) and temperatures ranging from 950 to 1200 K under fuel-lean to fuel-rich conditions.

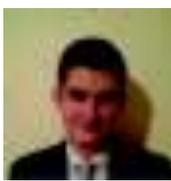


Main results

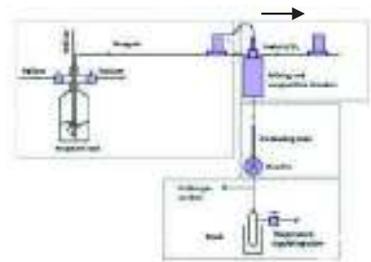
Methane oxidation temperature oscillation experiments were conducted in CO₂ as a bath gas with various methane mole fractions (0.01-0.05) under fuel-lean to fuel-rich conditions in a jet stirred reactor. The reactor temperature ranged from 950 to 1200 K, with residence time fixed to 2 s. Under fuel-lean conditions, the onset temperature of oscillation was 1050 K with methane mole fraction 0.01, it decreased to 1000 K with the increase of the methane mole fraction to 0.05. Under stoichiometric conditions, the temperature oscillation was initiated at 1100 K, when the methane mole fraction was 0.01. As the methane mole fraction increased to 0.05, the onset temperature of oscillation dropped to 1000 K. Under fuel-rich conditions, the temperature oscillation has two shapes: one peak and two peaks. The higher the methane mole fraction, the wider range the "two peaks". These data will be helpful to refine biogas detailed kinetic models.

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<p>2017</p> 	<p>Kinetic study of the gas phase pyrolysis of organic molecules containing heteroatoms. Application to the optimization of a soil remediation process by vacuum pyrolysis.</p> <p><u>Nicolas Vin</u> (2nd year), 2015</p> <p>F. Battin-Leclerc, O. Herbinet Axe 4 Terbis</p>	
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Keywords: soil remediation, pyrolysis, organic molecules, kinetic study, jet stirred and tubular reactor.

<p>General context, scientific issues</p> <p>Soil remediation becomes more and more important for the preservation of the environment and human health and the reuse of polluted areas. Several strategies can be used according to the nature of organic pollutants. Thermal desorption followed by thermal decomposition can be used for the treatment of pollutants such as hydrocarbon fuels, poly-aromatic hydrocarbons, or species containing heteroatoms (e.g. chlorine, sulphur).</p>	<p>Illustration:</p>  <p>Diagram of the apparatus used for the pyrolysis study</p>
<p>Objectives and stakes</p> <p>The objective is to study the pyrolysis of molecules with similar structure to pollutants. It is crucial to understand the chemistry of thermal decomposition of these pollutants to predict the influence of operating conditions on the nature and concentration of reaction products.</p>	<p>Main results</p> <p>During the second year, the pyrolysis of bromoethane has been studied in the jet stirred reactor. Chlorobenzene, nitromethane and diethylamine have been studied in a tubular reactor.</p> <p>The pyrolysis of bromoethane is controlled by an unimolecular reaction : Bromoethane is converted into hydrogen bromide and ethylene which are the main products. The molecule is completely consumed at 973 K (800 torr, 2s, molar fraction of 0.01).</p> <p>Chlorobenzene was nearly fully destroyed in the TR (95% of conversion) for an experiment at 800 torr, a residence time of 2 seconds and an inlet mole fraction of 0.005 at a temperature of 1250 K. The use of a tubular reactor inhibits the formation of aromatic products like biphenyl, biphenylene, chlorobiphenyls and dichlorobiphenyls.</p> <p>The Pyrolysis of nitromethane leads to a large formation of nitric oxide and methane, the main products. The molecule is fully destroyed at 825 K (800 torr, 2s, molar fraction of 0.01). Traces of NO₂, acetonitrile and hydrogen cyanide are observed.</p> <p>The Pyrolysis of diethylamine is more complex. It is leading to the formation of a lot of species. Methane, ethylene, ethane, hydrogen cyanide and acetonitrile are major products. The molecule is fully destroyed at 950 K (800 torr, 2s, molar fraction of 0.01).</p>
<p>Methodology / Experimental approach</p> <p>Two different reactors are used for this study: a jet-stirred-reactor (JSR) and a tubular reactor (TR, assimilated to a Plug Flow Reactor under our conditions). Experiments in JSR were performed at a constant pressure of 1.067 bar (800 torr), at a residence time of 2 seconds and at temperatures ranging from 800 to 1150 K. Experiments in the TR were performed at a constant pressure of 1.067 bar, at a residence time in the set-point temperature zone around 2 seconds and at temperatures ranging from 800 to 1300 K.</p> <p>The inlet gas leaving the reactors was analyzed using two gas chromatographs and a Fourier Transform InfraRed spectroscopy (FTIR) analyser via a heated transfer line maintained at 433 K to avoid product condensation.</p>	

<p>2017</p> 	<p align="center">Modeling of the spray process in the natural gas transport tank</p> <p align="center">Xiaochun Xu (Post-doc')</p> <p align="center">Jean-Noël Jaubert, Romain Privat Axe 4 ThermE</p>	
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Keywords: Liquefied Natural Gas, Spraying process, modeling, Equation of State

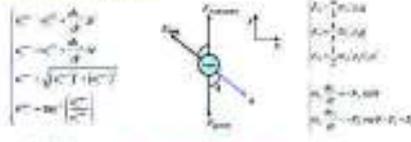
General context, scientific issues
 Natural gas is a flexible fuel that is used extensively for power generation, industrial and household consumption, as well as for the production of advanced petrochemical derivatives and it is expected to play a greater role in the future global energy mix. Natural gas can either be delivered by high pressure pipelines, or be liquefied, stored in bulk carrier and then transported by ship.

During the vessel transport of the liquefied natural gas (LNG), the gas phase in the tank normally could be cooled down by spraying the LNG with lower temperature.

Objectives and stakes
 In this work, the falling multi-component droplet evaporation model is developed for simulating the spray process.

Methodology / Experimental approach

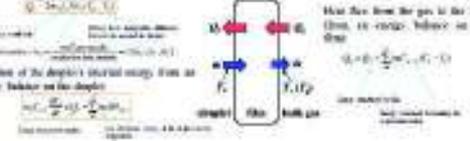
- Fall speed of a droplet**



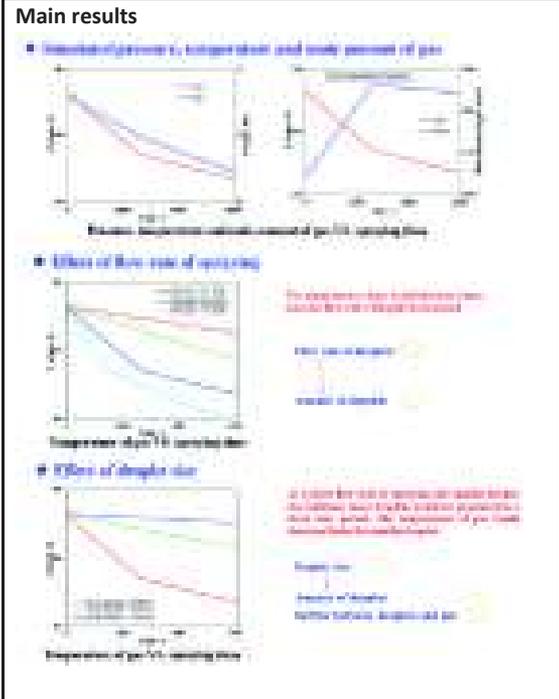
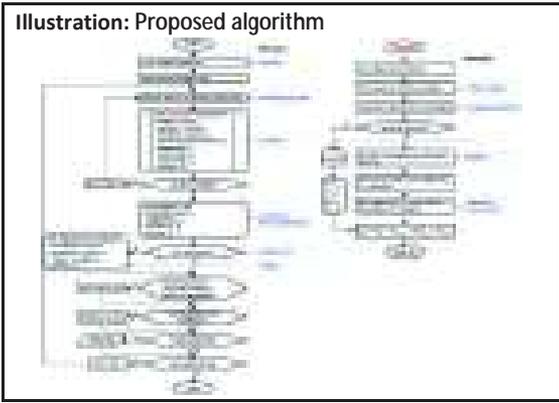
Drop velocity $U_d = f(\text{Re})$ with $\text{Re} = \frac{\rho_g U_d d}{\mu_g}$ and $\text{Bo} = \frac{\rho_g U_d^2 d^3}{\sigma}$
- Vaporized liquid fluxrate of component i (based on Hirschfelder's diffusion law)**



Mass flux of component i: $\dot{m}_i = 4\pi r^2 N_i (C_{i,s} - C_{i,\infty})$
- Heat flux between the gas and the droplet**



Heat flux from the gas to the droplet: $\dot{Q} = 4\pi r^2 h (T_g - T_s)$



References

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2017

Parametric optimization of Supercritical CO₂ Brayton cycle by MINLP approach



Qiao Zhao (LRGP, EDF)

Jean-Noël Jaubert, Romain Privat, Mounir Mecheri, Thibaut Neveux
Axe 4 | THERME | EDF R&D



Keywords: SC-CO₂, Brayton cycle, Equation of state, uncertainty, superstructure, optimization MINLP

General context, scientific issues

Efficiency enhancement in power plant can be seen as a key lever in front of increasing energy demand. Currently, both the attention and the emphasis are directed to searching for a reliable alternative, i.e., enhancing the energy conversion systems. Among different candidates, the supercritical CO₂ (SC-CO₂) Brayton cycle has emerged as a promising solution for high efficiency power production in nuclear, fossil-thermal and solar-thermal applications.

Objectives and stakes

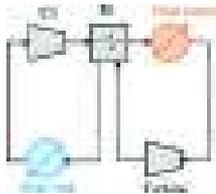
In order to achieve the industrial feasibility of this power cycle, non-linear optimization combined with process synthesis is identified as a powerful tool.

This thesis intends to describe a framework within consideration of a rigorous equation of state (EoS) for SC-CO₂ as well as an optimization-based synthesis of SC-CO₂ Brayton cycle, where superstructure-based optimization is employed. The simultaneous optimization of both the system structure and the process parameters is formulated as mixed-integer nonlinear programming problems (MINLP).

Methodology / Optimization guidelines:

- Selection and validation of a rigorous equation of state (thermodynamic model) for SC-CO₂
- Mixed-integer nonlinear optimization combined with process simulator

Equation of Span & Wagner (SW), Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Peng-Robinson with Boston-Mathias alpha function (PR-BM), Lee-Kesler-Plocker (LKP) and Benedict-Webb-Rubin modified by Starling (BWRS) are chosen to be evaluated in the process below.



MIDACO (Mixed Integer Distributed Ant Colony Optimization) solver is interlinked with ProsimPlus®.

Illustration:

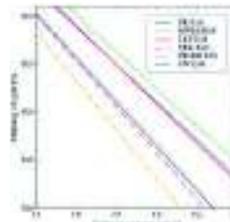


Figure 1: Results of pressure ratio sensitivity on efficiency for different equation of state. The straight line represents simulation points.

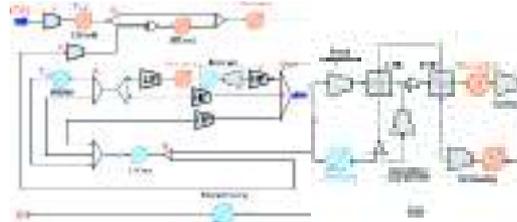


Figure 2: Defined superstructure for MINLP optimization and the optimized structure

Main results

In terms of pure-component behavior, among the 6 studied EoS, the Span-Wagner (SW) EoS is the one leading to the most accurate predictions of the CO₂ in the near-critical and supercritical regions. From a component-sizing point of view, it has been found that certain deviations can lead to over or underestimation of equipment costs.

Finally, it has been observed that the RC process optimization is also influenced by the EoS choice and can lead to 1%pt deviation on the predicted cycle efficiency depending on the considered EoS. Such a deviation has repercussions on the optimal operating conditions.

By combining the evolutionary algorithm and the penalty method, a global feasible optimum design –or at least competitive solutions– has been found given a process superstructure.

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PRODUCT ENGINEERING



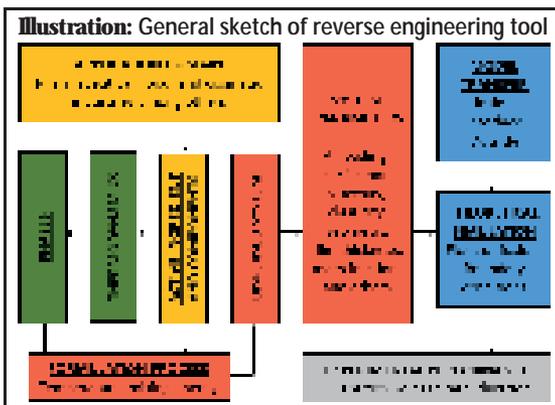
<p>2017</p> 	<p>MASS TRANSFER WITHIN COMPLEX MEDIA. REVERSE ENGINEERING : FROM FINAL TARGET PROPERTY TO MATERIAL</p> <p><u>Antonio Aguilera Miguel (3rd year)</u></p> <p>Christophe Castel, Véronique Sadtler, Philippe Marchal Axe 5 GEMICO </p>	
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Keywords: Product Design, Controlled Release, Highly Concentrated Emulsions, Computer Aided Molecular Design

General context, scientific issues
 In order to understand how something works, first we have to "disassemble it" and "figure out" their secrets. Only then, it will be possible to build something better. The process is called "Reverse Engineering" and in next future, enterprises will be depending on it to have access to the secrets of their competitors.

Objectives and stakes
 The purpose of my work is the development of a "Reverse Engineering" tool to be applied in formulation product design. This tool will help for the best choice of materials, as well as the most suitable set of formulation properties, in order to get a desired release rate, achieved for a specific active ingredient by using a specific delivery system. By means of this tool, product development can be accelerated, as well as time- and cost- intensive series of trial-and-error experiments are replaced. Main goals with the results of this work are focused on optimized product design and opportunities for processes intensification.

Methodology / Experimental approach
 From numerous materials providing interesting possibilities, emulsions have been all along identified as complex systems very flexible regarding composition, size distribution, phase equilibria, morphology and viscosity. Therefore, emulsions were chosen as a relevant model system for the experimental validation of this work. A development of physico-chemical models has been required to quantify mass transfer as function of product composition and structural parameters. Afterwards, appropriate computer aided molecular design techniques are employed to obtain the thermodynamic and geometric parameters required to predict the release curves of an active ingredient at different formulations. These modelling and simulation tools allow to rank generated systems versus an optimal target (zero order release for example). Expressed as a reverse design problem, the target property of a desired release reate becomes the input for design and only solutions more close to the specified target are tested experimentally.



Main results
 A study of a semi batch two-step emulsification process for obtaining highly concentrated emulsions was performed and deeper insight about formulation and structural parameters was gained. A programming code using the modified UNIFAC group-contribution method (Dortmund, 1993) was written in order to estimate activity coefficients of liquid-liquid mixtures. An additional algorithm was prepared for calculating distribution coefficients of a certain active ingredients within the emulsion phases. The thermodynamic descriptors were validated experimentally, and the mechanistic model has been successfully developed to consistently predict the diffusion of an active ingredient from the emulsion to a release medium in perfect sink conditions. A full factorial design of virtual experiments has allowed obtaining a quantitative description of the release depending on different variables. Real controlled release experiments have being carried out to check accuracy of predictions or possible limitations. Our methodology is showing to be of very high interest in the domain of formulation by allowing fast and robust screening preliminary studies on a broad range of components as well as rigorous prediction tools to optimize controlled release from an identified system.

References

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<p>2017</p> 	<p>Reinforcement of Polystyrene with Cross-Linked Particles and Study of the Kinetics of Free Radical Polymerization of Styrene in a 3D Network: an Application for Used Tire Rubber Recycling</p> <p>FLOREZ Daniela (2nd year)</p> <p>HU Guo-Hua, MEIMAROGLOU Dimitrios</p> <p>Axe 5 GP2</p>	
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Keywords: Ground tire rubber recycling, reinforced polystyrene, free radical graft polymerization, polymer composites, impact strength.

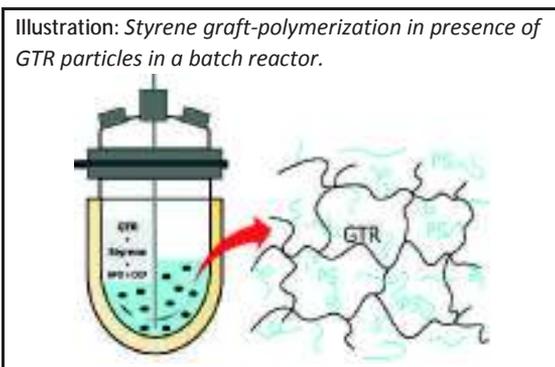
General context, scientific issues
 It is becoming increasingly difficult to ignore that worn tires wastes, disposal and accumulation is causing serious environmental problems worldwide [1]. Nevertheless, because of their composition and remarkable properties, they are widely recycled. Thus, tires are mainly composed of natural rubber/synthetic rubber blends (45%), reinforcing materials (20–28%), fillers and additives (27 -35%) [1].

Nowadays, waste tire rubber is ground to obtain small granules called GTR, which present a cross-linked molecular structure and are used as good mechanical properties modifiers in rigid polymer matrices. This idea is not only a promising strategy and economical method for reusing tire rubber, but also a solution for production of low-cost of composites [1]-[2].

Polystyrene (PS) is a thermoplastic, amorphous, colorless and brittle polymer. It is used for food packaging, disposable dishware, functional and decorative applications. PS is commonly reinforced with rubbers or rubber-copolymers to widen its scope of application and produce new goods of functional significance, but it is very expensive nevertheless [3].

Objectives and stakes
 This research project aims to develop a high strength PS composite by incorporation of GTR particles. Nevertheless, these phases are immiscible and their mixing represents a great challenge.

Methodology / Experimental approach
 In order to accomplish the objectives and create a composite with improved mechanical properties, this thesis involves two scientific approaches. On the one hand, the experimental approach aims to modify the surface of GTR by grafting styrene via free radical polymerization, to promote a complete adhesion between both phases GTR/PS. On the other, the modelling approach aims to develop a mechanistic model which leads to a better understanding of the chemical and physical phenomena taking action in the styrene bulk polymerization system in a batch reactor.



Main results
 Experimental results. Graft polymerization of PS onto GTR particles is an effective technique to combine these incompatible phases. Nevertheless, it is necessary to apply a second strategy to achieve a total interpenetration and thus enhance the final mechanical properties of the new composite material.

Modelling results. The model was developed (using MATLAB® software) on the basis of the comprehensive kinetic model for the combined chemical and thermal polymerization of styrene. It allows for the prediction of the polymer properties such as conversion, grafting rate and average molecular weight. Preliminary results, after validation with experimental data, suggest that the model and the kinetic model implemented are capable of describing the behavior of the polymerization system with good accuracy.

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2017 	PhD subject: Mn-doped Ag-In-Zn-S QDs as dual-modality probes for magnetic resonance and fluorescence imaging of cells <u>Perizat GALIYEVA (1st year)</u> Supervisor 1: Raphaël Schneider Supervisor 2: Halima Alem-Marchand Axe 5 EMMAD	
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Keywords: QDs synthesis, doped QDs, physico-chemical characterization, fluorescence, magnetism.

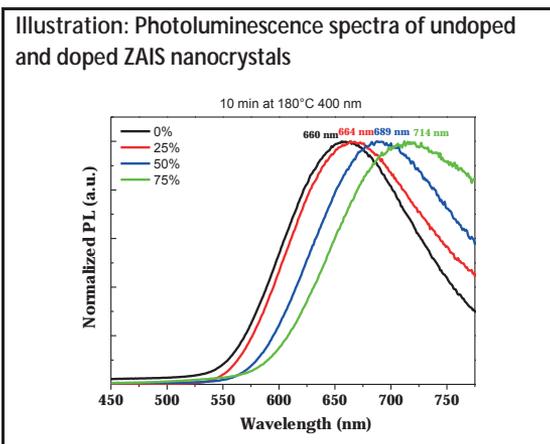
General context, scientific issues
 Ternary I-III-VI₂ semiconductors like Ag-In-S₂ and their alloyed Zn derivatives like ZAIS (Zn-Ag-In-S) quantum dots (QDs) exhibit a high potential for various applications like light-emitting diodes, lasers, solar cells, photocatalysis and molecular imaging. ZAIS nanocrystals possess remarkable optical properties (high photoluminescence quantum yields and stability) and their fluorescence can be tuned from the visible to the near-IR region [1].

Molecular imaging has stimulated intense interest as it will surely offer revolutionary tools not only for fundamental studies but also for biological and clinical applications. Integrating the advantages of different imaging techniques is apparently an effective approach for improving the efficacy of clinical imaging diagnosis [2]. In this work, the combination of optical imaging techniques and magnetic resonance imaging (MRI) will be evaluated to develop new probes for biomedical detections. Because of their luminescent and magnetic properties, Mn-doped ZAIS nanocrystals may be of high interest as alternatives to toxic cadmium-containing QDs.

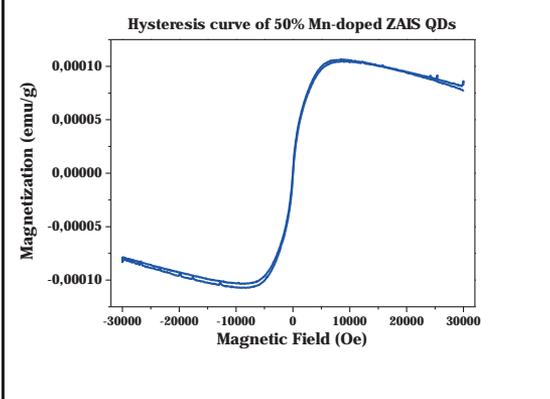
- Objectives and stakes
1. One-step synthesis of undoped and Mn-doped Ag-In-Zn-S QDs ;
 2. Physico-chemical characterization of QDs.

Methodology / Experimental approach

- Synthesis of Mn-doped Ag-In-Zn-S QDs with various dopant percentages.
- Physico-chemical characterization of synthesized QDs (optical properties, X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, magnetic properties,...).
- Aqueous dispersion of the dots and evaluation of these nanomaterials as bimodal probes for imaging.



- Main results
1. Mn-doped Ag-In-Zn-S and undoped Ag-In-Zn-S QDs can be prepared using a one-step synthetic method. The percentage of Mn dopant can be varied from 25 to 75% relative to (Ag + In + Zn).
 2. Mn-doped Ag-In-Zn-S QDs exhibit both fluorescent and magnetic properties.



References

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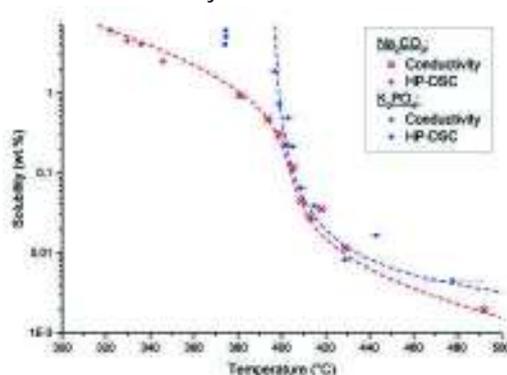
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<p>2017</p>  	<p>Thermohydraulic modelling of a continuous supercritical water oxidation process – incorporation of the precipitation of mineral species</p> <p><u>Gaëtan Lemoine (3rd year)</u> Hervé Muhr¹, Hubert-Alexandre Turc² Axe 5 EMMAD CEA (DEN/DE2D/SEAD)</p>	
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General context, scientific issues

Supercritical Water Oxidation (SCWO) is a promising technology for treatment of a wide range of mixed aqueous/organic industrial waste, among which nuclear radio-contaminated liquid waste. Under supercritical conditions ($P > 22.1$ MPa, $T > 374^\circ\text{C}$), water, organics and gases are completely miscible and fast and complete conversion of the organic matrix into CO_2 is achieved with yields greater than 99.9%. However, salt precipitation occurs when water is brought to supercritical conditions, what may cause plugging on continuous SCWO reactors.

Illustration: Solubility results



Objectives and stakes

In order to improve the efficiency of current SCWO reactors and to enhance the development of future ones, it is necessary to have a reliable numerical model of the process. Such a model limited to thermohydraulics and combustion chemistry has been implemented in previous studies [1]. The objective of this work is to develop a more complete model, able to predict inorganic salts behaviour inside the reactors.

Main results

Solubility data has been obtained for two different salts: Na_2CO_3 and K_3PO_4 . The results show two different trends, which are consistent with the classification established by Valyashko [2], that distinguishes two types of salts depending on their phase behaviours.

Regarding the results of the deposition experiments, salt deposits were indeed recovered and consequently analysed. The average size of the primary particles ($\approx 5 \mu\text{m}$) was determined by Scanning Electron Microscope observations. Furthermore, these experiments showed that the precipitation kinetics were very fast, therefore the assumption of an infinite precipitation rate may be used in the numerical simulation.

Some work has also been carried out concerning the choice of an equation of state suitable for the composition, temperature and pressure conditions of SCWO. The Volume-Translated Peng-Robinson equation have been chosen and then modified in order to fit experimental density data obtained by an *ad hoc* device.

Methodology / Experimental approach

The implementation of inorganic salts precipitation in the numeric model requires some experimental data, such as solubilities, precipitation kinetics or information on deposits morphology. Several experimental devices have been used to that purposes. The acquisition of the salt solubilities at hydrothermal conditions was done using two different static analytic methods: conductimetric measurements after precipitation in a high-pressure vessel, and high-pressure Differential Scanning Calorimetry. Then, deposition experiments were carried out in a continuous SCWO reactor. A specific procedure was applied in order to be able to recover the deposits formed by precipitation at high pressure and high temperature conditions. Using the same apparatus, mass balances were also achieved with the aim of assessing deposition kinetics.

References

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<p>2017</p> 	<p>Preparation and characterization of extruded synthetic- and natural-tannin resin composites</p> <p><u>Jingjing LIAO (2nd year)</u></p> <p>¹LRGP UL Nancy, France; ²Lermab, UL Nancy, France Axe 5 GP2 Processes for Products and Materials Process Engineering)</p>	
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Keywords: tannin resin, polypropylene, poly(lactic acid), composites, extrusion, 3D printing

General context, scientific issues

Tannin resin is widely used in wood bonding since long time. This project explores its possible applications as composite materials and its preparation through the extrusion process.

It aims to elaborate and characterize composite with tannin resin based on plastic matrix, especially the degradable plastic such as poly(lactic acid). This totally eco-friendly tannin resin can be also interesting for 3D printing.

Objectives and stakes

1. Elaboration and characterization of polypropylene/tannin resin composites.
2. Elaboration and characterization of poly(lactic acid)/tannin resin composites.
3. Use of poly(lactic acid)/tannin resin composites for 3D printing.

Methodology / Experimental approach

1. Mimosa tannin prepolymers are prepared in a stirred reactor fitted with a reflux condenser. The mimosa tannin extracts are dissolved in water and NaOH is added to adjust its pH to 10. Tannin solution is heated to 80 °C during half of an hour, then 6 parts of hexamine is added into the mixture. All the compounds are added based on the weight of the dry tannin. After the given reaction time, mimosa tannin prepolymers are diluted with water. Then, all the water was removed by dry spray.
2. Preparation of tannin resin/PP composites are conducted in a twin-screw extruder. All the elements are mixed at certain proportions in a baker before injection into the extruder. The screw rotation speed is 200 rpm and the barrel set temperature is 190°C. The extruder is equipped with highly efficient vacuum venting to remove unreacted species and reaction by-products. The extrudate is pelletized by a grinder.

Illustration: The process of the experiment



Main results

- ✓ The elaboration and characterization of polypropylene/tannin resin composite are successfully carried out. These composites have high Young modulus strength and breaking strength compared with neat polypropylene.
- ✓ Tannin resin particles are dispersed into polypropylene mainly as particles with a diameter between 5 to 20 micrometers, even at high concentration.
- ✓ A decrease in storage modulus(G') and loss modulus(G'') is observed with the increment of tannin resin as well as the complex viscosity. This might probably because of the tannin resin can reduce the deformation force.
- ✓ Tannin resin slightly decreases the melting point and no significant effect on crystallization is observed.

References

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<p>2017</p> 	<p>Design and multi-criteria optimization of an extrusion process for the manufacture of nanocomposites based on recycled polymers reinforced by cellulose nanocrystals</p> <p><u>Karen Mariana MANCERA GARCIA (3rd year)</u></p> <p>Sandrine HOPPE¹, Fernand PLA¹, Vladimir ESCOBAR²</p> <p>¹LRGP UL Nancy, France; ²IPICYT, San Luis Potosi, Mexique</p> <p>Axe 5 GP2 Processes for Products and Materials Process</p>	
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Keywords : Cellulose nanocrystals, nanocomposites, recycling, extrusion, multi-criteria optimization

<p>General context, scientific issues</p> <p>This project enters within the framework of the valorization of recycled polymers, which are generally degraded during the processes implemented for their recycling.</p> <p>It aims proposing original solutions allowing to re-use, at a lower cost, those second generation products, thanks to their transformation/inclusion in formulations allowing to create new materials.</p> <p>Due to their industrial importance and attractiveness, recycled polyethylene terephthalate (PET) and low density polyethylene (LDPE) were chosen, with the objective of manufacturing, by melt extrusion, stable compatibilized PET/LDPE blends reinforced by crystalline nanoparticles of cellulose (CNCs) which structure, mechanical and rheological properties, together with renewability and</p>	<p style="text-align: center;"><u>CNCs characterization (TEM)</u></p>  <p style="text-align: center;">(Aver. length 110-150 nm ; Aver. thickness: 5-8nm)</p> <p style="text-align: center;"><u>Synthesis of reinforced nanocomposites</u></p>  <p style="text-align: center;"><i>Extrusion and granulation</i></p>   <p style="text-align: center;"><i>Injection molding</i> <i>Blends samples</i></p>
<p>Objectives and stakes</p> <ul style="list-style-type: none"> • CNCs synthesis and surface modification • Synthesis of a compatibilizer based onSEPS, PAA and CNCs. • Manufacturing by melt extrusion, of • recycled reinforced PET/LDPE. 	<p>Main results obtained until now :</p> <ol style="list-style-type: none"> 1. The synthesis and characterization of the IPN were successfully carried out. This IPN exhibit adequate affinity with PET, LDPE and hydrophobized CNCs. It acts as a plasticizer giving rise to materials with high elongation at break. PAA of IPN interacts with PET and CNCs. 2. CNCs surface hydrophobization was obtained by 2 methods: (i) PEO deposition and (ii) esterification with organic acid chloride aliphatic chains of different sizes. (e.g. hexanoyl, lauroyl and stearoyl chlorides).
<p>Methodology/ Experimental approach</p> <p>Two key scientific problems must be solved :</p> <ol style="list-style-type: none"> 1. The CNCs surface hydrophobization in order to improve their dispersion in PET and LDPE 2. The synthesis and the characterization of a multifunctional compatibilizer able to stabilize the blends morphology. We choose preparing an interpenetrating network (IPN) composed of crosslinked polyacrylique acid (PAA) partially esterified by CNCs and distributed in a bloc copolymer (SEBS) 	
<p>Next work:</p> <ol style="list-style-type: none"> 1. Development of an experimental strategy to study the effect of the process parameters on the morphology and the mechanical properties of the blends 2. Modeling and multicriteria optimization of the whole process 	
<p>References</p> <ul style="list-style-type: none"> • Habibi Y., Dufresne A., Biomacromol. 2008. 9, 1974–1980. • Ljungberg N., Bonini C., Bortolussi F.; Boisson C., Heux L., Cavaille J. Y. 2005. Biomacromol. 6, 2732–2739 • Rebouillat S., Pla F., J. of Biomat. and Nanobiotech.. 2013. 4. 165-188 	

2017 	CDD subject: Development of a software tool integrating the stages of the design of experiments with the modelling and optimization of the processes in a single generic simulator. <u>Maria Meimaroglou (Ingénieur de recherche)</u> Supervisor 1 Sandrine Hoppe, Supervisor 2 Dimitrios Meimaroglou Axe 5 GP2	
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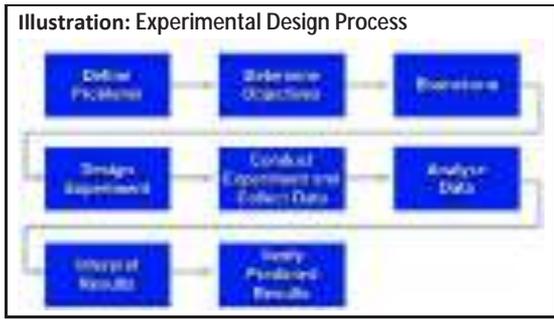
Keywords: Design of experiments, modelling, factorial experiments, response surface methodology

General context, scientific issues
 The general context of this study is the conception and development of a generic simulator which combines the field of the design of experiments (DoE) with the modelling of the processes.

Objectives and stakes
 The objective of this work is the complete bibliographical survey of the methods used for the DoE that can be applied to different problems of process engineering, along with the examination of the software already developed and used for those purposes. On a second stage, the preliminary conception of the part of the simulator that corresponds to the decision making process, resulting in the selection of the appropriate method according to the type of the problem, is envisaged.

Methodology / Experimental approach
 The study includes a complete bibliographical review and analysis of the different methods used for the design of experiments. The main characteristics of different DoE methods will be extensively studied and enlisted. A specific categorization will also be attempted on the basis of criteria related to the types of the problems that each method is most suitable for, as well as their main advantages and limitations.

The study will be completed by an extensive testing, comparison and evaluation of existing commercial software on the field of DoE, at different levels including their interface, ease of operation, selection of methods, analysis of results and the help provided during the planning of the design and the analysis of the results. The aim of this part of the work is to investigate whether the existing commercial software can respond to the needs of a researcher that requires a basic guide on the process of experimental design, but has no prior knowledge on the field.



Main results
 The different methods employed for the DoE have been classified firstly according to the demanded experimental objective into the categories of *screening*, *optimization* and *robustness* testing and, secondly, according to the mathematical model selected to relate the response variable with the factor effects. A complete summary table has been constructed presenting the general characteristics of the reviewed methods, including the *number of experiments* demanded by each method, the *number of levels* admitted for each *controllable factor*, and, finally, their *suitability* concerning the aim of the DoE (i.e., the experimental objective and the appropriate model). Besides the above criteria, related to the design process, the present study has also covered the post-design process, namely the *analysis of the results* and the *eventual need for relevant changes in the initial design*. Finally, a comparative study has also been carried on existing commercial software with respect to their level of guidance and completeness in terms of the above mentioned DoE aspects.

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2017	Transitional Phase Inversion Emulsification with Surfactant Copolymers		<p><u>Martin Meulders (1st year)</u> Cécile Nouvel, Véronique Sadtler Axe 5 PPM</p>	
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Keywords: Transitional Phase inversion, Conductivity, Copolymer surfactant, Emulsification, Phase Inversion Temperature

General context, scientific issues

Nanoemulsions (droplet size from 20 to 200 nm) have many interesting properties relatively to macroemulsions: an optical transparency, a greater stability against coalescence and creaming but above all a greater exchange surface. Unfortunately, their formation traditionally requires high-energy techniques such as high-pressure homogenization. The Phase Inversion Temperature emulsification method (PIT) is a low energy process to produce nanoemulsions [1]. This phenomenon relies heavily on the architecture of the surfactant and only small surfactants have been widely studied until now.

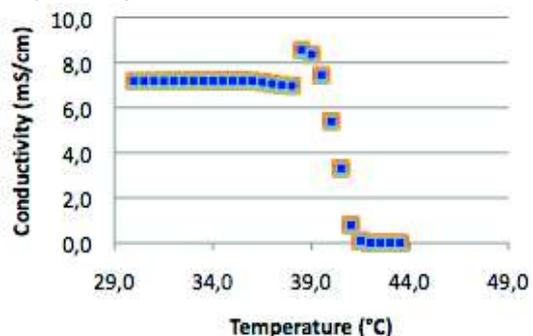
Objectives and stakes

The aim is to determine the emulsification conditions through PIT method with polymer surfactant as stabilizer to obtain nanoemulsions. So far, no large polymeric surfactant was used in the literature to obtain nanoemulsions thanks to this emulsification mechanism. Therefore, we must understand the impact of the polymer structure on the phase inversion mechanism and determine the limitation of macromolecular surfactants for their ability to produce efficiently nanoemulsions with the PIT technique.

Methodology / Experimental approach

- 1) Creation of the experimental setup for the emulsification process by phase inversion temperature method:
 - Determination of the critical parameters for the PIT emulsification using any surfactant available [2][3]
 - Evaluation of commercial polymers as surfactants
- 2) Design and synthesis of copolymer surfactants for their application in PIT emulsification method
- 3) Realize nanoemulsions through PIT with copolymer surfactants
- 4) Study the impact of composition and the (co)polymer structure in order to define in details the relation between their composition/structure, their ability to allow emulsification by the phase inversion method and the resulting properties of the nanoemulsions produced.

Figure 1 : Conductivity profile during a phase inversion temperature procedure



Main results

Several commercial surfactants including an ethylene oxide part have been tested with the same system dodecane-water for a wide range of surfactant concentrations. Commercial products belonging to the Brij® family were used as model of low molecular surfactants. Triblock copolymer surfactants (Pluronic type®) were tested for the PIT procedure to study the impact of the size of the surfactant.

- The PIT procedure carried out with different Brij® as surfactants led to fine and stable nanoemulsions (average droplet size around 95 nm, stability > 2 months)
 - Some triblock copolymer surfactants (Pluronic®) were tested in PIT emulsification to study the impact of the size of the surfactant
 - The first assays of PIT emulsification carried out with the most efficient Pluronic® did not lead to achieve stable emulsion. However a beginning of transitional phase inversion was observed.
- Nevertheless, these results are promising to prepare nanoemulsions with this method.

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2017



New Heterostructured ZnO/C₃N₄ Materials. Application to Solar Photocatalysis

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Schneider Raphaël
Axe 5 | EMMAD



Keywords: Photocatalysis, ZnO rods, solar/visible light, C₃N₄, photocatalyst, ZnO/C₃N₄, Orange II dye.

General context, scientific issues

Our objective is to demonstrate the advantages of coupling ZnO nanorods with graphitic carbon nitride (C₃N₄) to improve photocatalytic reactions.

ZnO nanorods, and in especially rods with a length lower than 250 nm, possess excellent photocatalytic activity due to their high surface area and their high stability. However, like most semiconductor oxides used in photocatalysis such as TiO₂ or ZrO₂, ZnO suffers from two major disadvantages:

- It can only be effectively excited with UV radiation due to its bandgap energy of 3.37 eV,
- The recombination of charge carriers (electrons and holes) is very fast and the number of these charge carriers really useful in the photocatalysis reactions is therefore very low.

One of the strategies developed in recent years to improve the photocatalytic efficiency of ZnO is its association with carbonaceous materials such as graphene or graphitic carbon nitride C₃N₄ [1-2]. Due to their conductive properties, these materials will "trap" the photo-generated electrons after light excitation, decrease the electron/hole recombination and thus allow an improvement in photocatalytic efficiency.

Objectives and stakes

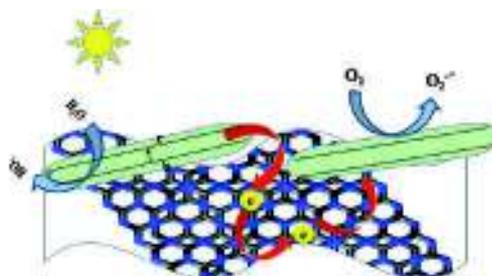
- Develop a new solvothermal method for associating small ZnO rods to C₃N₄.
- Characterization of ZnO/C₃N₄ composites.
- Evaluation of the photocatalytic performances of the ZnO/C₃N₄ materials in the degradation of the Orange II dye under solar or visible light.

Methodology / Experimental approach

The work is divided into 2 parts:

- Synthesis and characterization (UV-visible and fluorescence spectroscopies, TEM, XRD, DLS,...) of ZnO rods and ZnO/C₃N₄ heterostructured catalysts.
- Evaluation of the photocatalytic performances and of the stability of ZnO/C₃N₄ materials.

Illustration: Possible mechanism for the degradation of Orange II with the ZnO/C₃N₄ catalyst under simulated solar light irradiation.



Main results

ZnO nanorods (with an average length of ca. 70 nm and a diameter of ca. 8 nm) associated to C₃N₄ were synthesized using solvothermal method (EtOH, 160°C). The photocatalytic performances were found to depend on the amount of C₃N₄ associated to ZnO. The ZnO/C₃N₄ composite with 10 wt% C₃N₄ allows the highest removal of Orange II (99% of degradation under solar light irradiation after 120 min, intensity = 5 mW/cm²). Moreover, the ZnO/C₃N₄ photocatalyst was found to be weakly sensitive to salts commonly present in wastewater and to pH changes and could be reused up to 10 times without significant loss of catalytic activity. The increased light absorption in the visible range and the reduced charge recombinations originating from the association of ZnO rods with C₃N₄ are responsible for the highest catalytic activity of the ZnO/C₃N₄ composite compared to ZnO rods. We hope that the solvothermal method developed in this work for the production of high quality ZnO rods associated to C₃N₄ is a promising technique for the preparation of efficient photocatalysts.

References

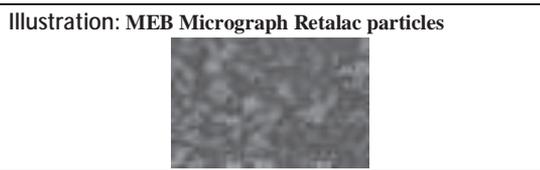
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2017 	Powder rheology : measurement systems, modeling and formulation <u>Assia SAKER (2nd year)</u> Véronique FALK, Philippe MARCHAL Axe 5 EMMAD I Processes for Products and Materials	
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Keywords: Powder technology, Powder flow, Storage, Flowability, Formulation, Powder rheometer, Atomic force microscope AFM, Densification , Particle size distribution, Energy of tapping, Energy of vibration, Packing behavior.

General context, scientific issues

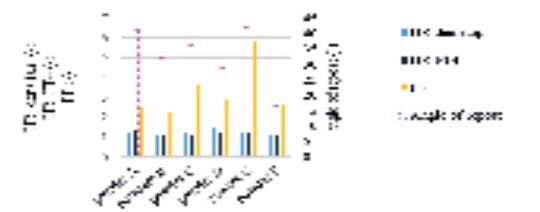
In many industrial pharmaceutical sectors, food and cosmetic industries, products are manufactured in powder form. Handling, storage, packaging ... require great control of flowability. Poor flowability is drastically linked to products losses on an industrial scale, thus its control by the study of powder properties is essential. The flowability of powders is related to both intrinsic parameters such as shapes, particles sizes and extrinsic parameters like humidity and temperature. In this thesis, our study focuses on the overall understanding of technological tools to propose an experimental methodology and a predictive mathematical model of the flow of bulk materials.



- Objectives and stakes**
- ✓ Understand the interactions between particles and between particles and equipment.
 - ✓ Achieve a multi-scale characterization of flowability and rheological behavior of powders.
 - ✓ Measure the interactions between powder/powders or powders/tip by AFM technology.
 - ✓ Explain, the change in flowability classification according to the different techniques.
 - ✓ Access to packing properties by various techniques available in the laboratory.
 - ✓ Transpose to industrial scale.
 - ✓ Develop a predictive model of powder flowability.

Main results

The transition from one technique to another significantly changes the ranking of the flowability since each technique subjects the powders to very different mechanical stresses. Therefore, each technique should be used in consistency with the mechanical conditions encountered in a particular application.



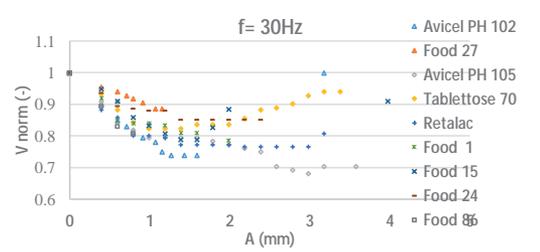
One of our techniques, allowing the control of mechanical vibrations, clearly shows that, depending on the working parameters (amplitude A and frequency f), the classification of the flowability may be reversed. Current work shows an interdependence between the initial state of powders and their physicochemical characteristics, however, the flowability of powders in our work is closely related to work settings.

Methodology / Experimental approach

To study the effects of shapes and sizes, a wide range of pharmaceutical, cosmetic and food powders was selected. Powder characterization is carried out from the analysis of the particle size distribution using laser granulometer Mastersizer 2000 and of the powders morphology by imaging with a scanning electron microscope.

The characterization and classification of flowability of powders are usually based on angle measurements or packing properties. One aim of the project is to obtain powder flow properties by using powder rheometers.

Promising technologies such as AFM (atomic force microscopy), allow to visualize powders surfaces, estimate their roughness and obtain 3D images but also to access to interaction forces measurements necessary to understand their large impact on flowability. These measurements will fulfill the study.



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<p>2017</p> 	<p>Study and Modeling of the influence of the physicochemical properties of concentrated suspensions on their rheological behavior</p> <p><u>Fabien Sta (3rd year)</u></p> <p>Philippe Marchal, Cécile Lemaitre, Christophe Boulnois Axe 5 GEMICO Nexter Munitions</p>	
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Keywords: Rheology, concentrated suspensions, Design of experiments, physico-chemical properties

General context, scientific issues
 Nexter Munitions is the European leader in the fields of the melt-cast process [1]. This process consists in obtaining a homogenous biphasic concentrated suspension by mixing a melted energetic binder with granular materials. The obtained formulation is then poured by gravity into shells. In order to develop new products with a limited number of experimentations, Nexter Munitions wishes to deepen its knowledge of the concentrated suspensions rheology, and particularly the one of fusible explosives. Indeed the rheology of concentrated suspensions is still accurately studied in various industries, because of the rheological complexity of this type of mixture [2] [3].

Objectives and stakes
 In this context, this work aims at relating the physicochemical properties of the solid phase to the rheological behavior of the main explosive charge. More generally, the objective is to link the structural properties of the suspension, at a microscopic scale, to its thermo-mechanical behavior, at a macroscopic scale. This goal will be reached by adopting an experimental approach, followed by mathematical modelling.

Methodology / Experimental approach
 The first step of the study was to establish a rheometer methodology to study the suspensions, to characterize their rheological behavior and to acquire relevant rheological information. As all the previous studies on the mixture seemed to show a time dependant behavior, the dedicated methodology was designed to take into account both the measurement time and the imposed shear rate. Moreover, the physicochemistry of both the liquid and granular parts of the studied mixtures were characterized. The final step of this work to link those characterizations to the rheology of the formulations, through a Design of experiments. The objective was to highlight which component(s) is(are) the most discriminating considering the casting time of the studied formulations. Once this step accomplished, the rheology of the concentrated suspensions was correlated to the significant physicochemical properties of their components through a structural model.



Main results
 As stated previously, the suspensions were firstly characterized. This first step highlighted the fact that the studied mixtures present a rheology which is shear thinning and time dependant. The characterization of the constituents was then made, in order to link them to the rheology through the Design of Experiments. The Design of experiments, for its part, allowed to mathematically determine the components which significantly impact the rheology of the suspensions. Those mathematical results were confronted and explained with the literature, in order to confirm they are really correlated to the rheology and that they do not stay theoretical values with no "physical reality". The liquid part of the suspensions was also studied. Upon humbly participating to the structural network of the suspension (through its droplets in suspension in another liquid), its viscosity has to be known in order to fully determine the fluid one. Indeed, an exponential model was chosen to model the rheology of the fluids. The model also contains the viscosity of the liquid part which follows an Ostwald de Waele (power law) equation. Finally, the exponential contains the equation which links rheology and physical chemistry (obtained through the DOE). Moreover, verified through deformation, this model is also predictive by giving an accurate viscosity when the solid fraction varies even if it was made for a specific constant one.

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2017 	Synthesis processes, properties and applications of bio-based engineering elastomers <u>XINXIN ZHOU(2nd year)</u> GUO-HUA HU, LIQUN ZHANG Axe 5 GP2 Processes for Products and Materials	
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Keywords: Synthesis, properties, engineering applications, bio-based elastomers, green tires, green chemistry, nanocomposites, sustainable development

General context, scientific issues

Globally, we are facing a massive growth in the number of urban vehicles. This growth comes at the cost of enormous fuel consumption, CO₂ emissions and air pollution. Tires are an essential component of all urban and rural vehicles. Synthetic elastomers used in tires now are mainly derived from petrochemicals, which are not sustainable. The global climate change (global warming) and air pollution (smog or haze) strike directly at the intersection of societal environmental demands and economic needs. Environmentally-friendly solutions must be found. To meet this target, renewable elastomers must be developed and non-renewable carbon black must be replaced with non-petroleum-based fillers, like nano-silica.

Objectives and stakes

The objective of this project is to fabricate low roll-resistance green tire elastomers from large-scale, bio-based chemicals, specifically itaconic acid, mono-alcohols and conjugated dienes.

- Itaconates were prepared by esterification of itaconic acid using the mono-alcohols.
- Bio-based elastomers were synthesized through redox emulsion polymerization of itaconates and dienes.
- Novel green tires were fabricated by combining molecular design of bio-based elastomer and *in-situ* modification technology of silica.

Methodology / Experimental approach

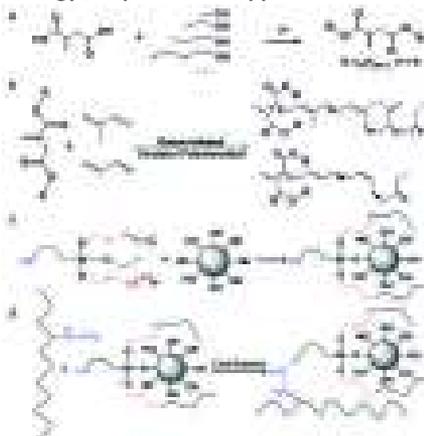


Illustration: The integrated bio-based chemicals-synthesis-low roll-resistance green tire pathway for resource sustainability and environment protection.



Main results

The present approach is sufficiently general to open the way to bio-based engineering elastomers that combine the advantage of fast-developing renewable chemicals and traditional synthesis methods. The properties of bio-based elastomers can be tuned by using different aliphatic alcohols or changing isoprene to butadiene. Silane-modified silica was used to reinforce the bio-based elastomers to form uniformly dispersed and strong silica-polymer interactive nanocomposites which offered superior mechanical properties and exhibited low energy consumption. Combining bio-based chemicals and *in-situ* modification technology to develop green tires is an important step in the global strategy for sustainable development.

Poly(dibutyl itaconate-*co*-butadiene) (PDIB) elastomer together with *in-situ* modification technology led to the best improvement in roll-resistance and wet traction without any compromise in tread wear. The silica/PDIB tire was manufactured and tested in Linglong Tire Co., Ltd using a MTS tire roll-resistance measurement system. The roll-resistance coefficient was 7.7 kg/t and rated as a 'B' level according to the EU Tyre Labelling Regulation 1222/2009, which is a high level since class A is still few in the European market.

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