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REACTIONS AND



REACTIONS ET GENIE DES PROCEDES
CHEMICAL ENGINEERING LABORATORY

Presentation of PhD and Post-doctoral research works at LRGP

JULY 1st, 2015

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 as of July 1th 2015 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 and Products
- 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

Processes For Environnement, Safety And Ressource Valorization



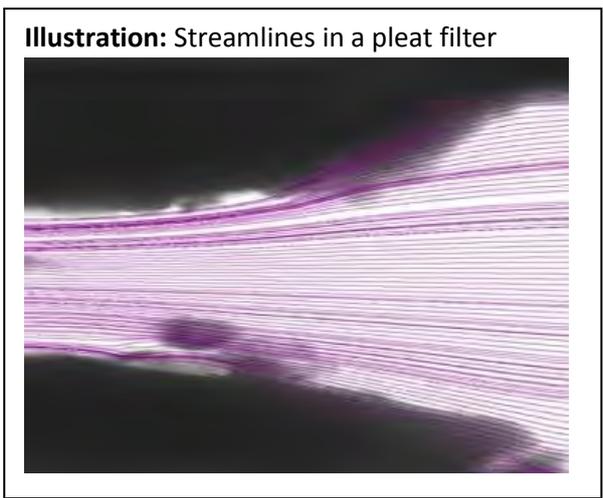
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REACTIONS ET GENIE DES PROCEDES
CHEMICAL ENGINEERING LABORATORY

<p>2015</p> 	<p align="center"><u>Impact of airflows induced by the filter media pleating on clogging phenomena for steady and transient states</u></p> <p align="center">ALILOU Youssef (1st year)</p> <p align="center">Supervisor: THOMAS Dominique¹, BARDIN-MONNIER Nathalie¹</p> <p align="center">LRGP, SAFE</p>	
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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 increase rapidly due the loss of filtration surface, this phenomenon is called surface reduction; 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 predicted models of clogging in both regimes transient and permanent one.

Main results:
 The first obtained results concern the clean filter pleat. Introducing filtration surface loss due to pleat deformation leads to a good estimation of pressure drop for low and median filtration velocities. μ -PIV method has been adapted to measure the velocity field inside the filter for different filtration velocities at the first instants of the experience to avoid clogging. Flow has been seeded with DEHS particles ($0.01 < Stk < 0.05$). The first results are used to validate airflow numerical simulation. In future, tomography technic will be used to enhance the comprehension of the deformation phenomenon and to have real geometry to simulate clogging on it.

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 inside the filter. In fact particle deposit is largely influenced by the flow nature and geometric changes [1]. Using an experimental device composed of a single pleat of the filter, PIV technics is used to measure flow in it and the results will be used to validate numerical models for pressure drop. Secondly, we will look to clogging phase. We will begin by characterizing the particle deposit inside the filter, using tomography technics and MEB visualization. We will realize a grid tests based on different filtration velocities and aerosols types. Numerical models will be enhanced and validated upon grid tests.

References:
 [1]: R. J. WAKEMAN, Chemical Engineering Research and Design, 83(A10): 12461255

2015



Can bubble columns be an alternative to fibrous filters for nanoparticles collection?

Maria Cecilia CADAVID RODRIGUEZ (2011-2015)

Dominique THOMAS, Augustin CHARVET
LRGP, SAFE



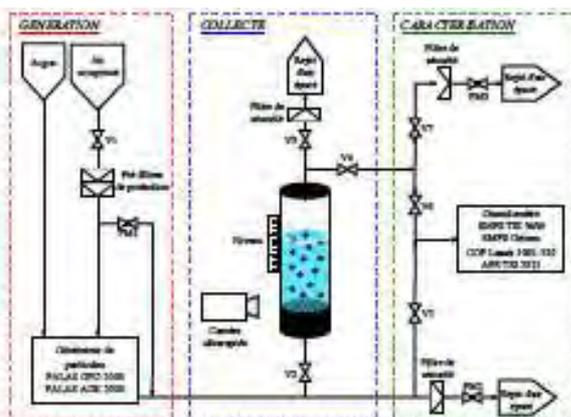
General context, scientific issues

The most effective and widely used dust separation techniques to separate ultrafine particles of a carrier fluid are fibrous media. The main problem is the clogging of the filter that induces a pressure drop increase over time and thus requires a regular cleaning of the media (or its replacement). In this context, the idea is to test bubble columns, which operate at a constant

Objective

- develop a new filtration process
- test its performances

Illustration:



Main results

This study proposes to investigate the influence of different operating conditions such as the liquid level, the air flow rate, the bubble size and the presence of beads, on the collection of ultrafine particles. Despite collection efficiencies lower than those of fibrous filters, experimental results show that bubble columns present high collection efficiency when the liquid level is high and bubbling orifices have low diameters. Besides, if gas velocity does not show an important influence on the collection efficiency, the presence of beads in the liquid increases the residence time of the bubbles in the column and thus the collection efficiency.

For more information

CADAVID-RODRIGUEZ Maria-Cecila, , *Les laveurs: une alternative aux médias fibreux pour le traitement des nanoparticules issues des fumées de métallisation?*, Doctorat Univ. Lorraine, RP2E, 10 mars 2015

CADAVID-RODRIGUEZ M.C., CHARVET A., BEMER D., THOMAS D., *Optimization of bubble column performance for nanoparticle collection*, Journal of Hazardous Materials, 271, 24-32 (2014)

CADAVID-RODRIGUEZ M. C., CHARVET A. , BEMER D., THOMAS D., *Les colonnes à bulles : une alternatives aux médias fibreux vis à vis des nanoparticules ?* 9^{ème} Congrès Francophone de Génie des Procédés, 28-30 avril, Agadir, Maroc (papier N° 324 / CD Rom) 8 pages (2014)

CADAVID-RODRIGUEZ M.C., CHARVET A., BEMER D., THOMAS D., *Intensification of nanoparticles collection efficiency in a bubble column*, FILTECH 2013, Wiesbaden, 22-24 Octobre 2013, Ref G02-03-008 (in CDrom), 9 p, ISBN 978-3-941655-07-2

CADAVID-RODRIGUEZ M.-C., CHARVET A., BEMER D., THOMAS D., *Une solution alternative aux médias fibreux pour la collecte de nanoparticules*, XIV^{ème} Congrès de la Société Française de Génie des Procédés - Lyon, 8-10 Octobre , Récents Progrès en Génie des Procédés, Numéro 104, ISBN 978-910239-78-7, Ed. SFGP, Paris, France (CD rom) (2013)



Design, modeling and development of a process for removing formaldehyde in indoor air

Anaëlle Cloteaux (3rd year)

Dominique Thomas, LRG P - Safe
Jean-Claude André, CNRS



General context, scientific issues

In the service sector, nearly 10 million employees work in an office in France. The measurement campaigns carried out in office buildings regularly reveal some formaldehyde concentrations higher than the values recommended by the Observatoire de la Qualité de l'Air Intérieur. The presence of this cancerogenic compound in indoor air is explained by its abundant use in furniture and decoration materials. In the current energy saving context, this situation is accentuated by an enhanced building insulation and an increase in the control over air renewal rate.

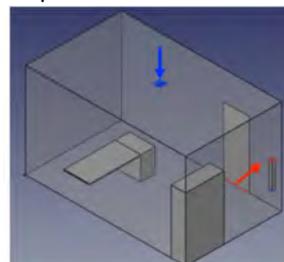
Objectives and stakes

The objective of this work is to design a purification process, clean, safe and able to remove the traces of formaldehyde in the indoor air.

Methodology/ Experimental approach

The stand-alone air purifiers have the advantage of being adapted to all types of buildings: either unventilated, or naturally and mechanically ventilated. The first stage of this work consists in studying the relevance of the installation of such a device in indoor air. The numerical simulation of airflow in an office is used to evaluate the *a priori* efficiency of a stand-alone device. This study identifies the parameters (flow and efficiency) for which the pollutant concentration in the room is significantly reduced. The purifiers, currently available, directly treat the ambient air by technologies involving incomplete reactions. As a result, degradation by-products, sometimes more toxic than the original pollutant, are found in the air. In order to provide a system dealing with with the fundamentals of sustainable development, the technology chosen must trap and degrade the major and minor pollutants at the same time. After an evaluation of possible technologies, absorption coupled with photocatalysis in liquid phase seems to be the most satisfactory solution.

Illustration: Perspective view of the studied office



Main results

Having demonstrated the ability of photocatalysis to degrade the formaldehyde, the next step consists in testing the degradation of toluene by photocatalysis. The degradation of this indoor air pollutant, with is found to be more complex and more stable than formaldehyde, also provides information on the limits of the selected process. By operating in a closed system, it is possible to degrade complex molecules and their by-products by photocatalysis. The advantage of using liquid phase, allowing the accumulation of the pollutants, is then highlighted compared to the direct treatment of the ambient air. To overcome the eventual release of catalyst particles in the ambient air, a packing consisting of Raschig rings impregnated with titanium dioxide is designed. Its effectiveness is evaluated in a fixed bed reactor. In order to obtain the kinetic law, this reactor requires the development of a model which takes into account at the same time the hydrodynamics of the system, the mass transfer in the liquid phase and the photocatalytic degradation on the surface of the catalyst. This fixed bed photocatalytic reactor is then coupled with an absorption column to constitute a pilot device able to degrade a continuous flow of formaldehyde. Its efficiency to treat the effluent that is generated in the laboratory scale is compared to that predicted by the mathematical model. The last step of this work is to examine the feasibility of a cleaner operating in the same way that the laboratory pilot to test air purification in real situations. The system sized from developed models was found to have a small volume. An efficient, compact, quiet and attractively designed device is an advantage for this air purification solution to be accepted and adopted by users.

2015



Combustion-turbulence interactions in dust explosions and hybrid mixtures flames

Nicolas Cuervo (4th year)

Olivier Dufaud, Laurent Perrin
SAFE



General context, scientific issues

Hybrid mixtures, mixtures of fuels and oxidizer in which the fuels are combustible dust mixed with flammable gas or vapour, are encountered in numerous industries. Gas/dust explosions have been studied for years [1], but very few researches have been carried out on the hydrodynamic behaviour of such flames.

As regard to gaseous mixtures, the presence of particles strongly modifies the turbulence level of the initial cloud but also the flame stretching during its propagation. The fundamental characteristics of the flame and the limiting steps of the explosion process are then different.

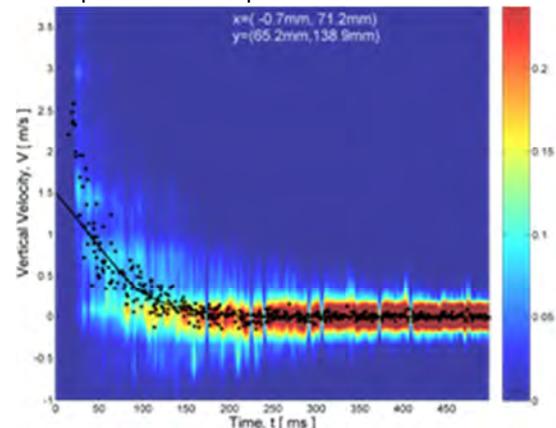
Objectives and stakes

This study will lead to the classification of such turbulent flames as a function of classical parameters such as the turbulence scale and intensity, the flame thickness and stretching factor. These results will be used to adjust and improve the models for the simulation of such non stationary turbulent combustion processes. They will also allow a better determination for flame quenching conditions and barriers

Methodology/ Experimental approach

Experiments have been performed by PIV to characterize the turbulence in the initial gas/dust cloud. In parallel, pyrolysis tests (flash pyrolysis and GC measurements) have been carried out to determine the rate-limiting step of the dust explosion. Moreover, dust (e.g. starch), gas (e.g. methane) and hybrid explosions have been performed in the 20 L sphere. Finally, the flame propagation has been studied in a 5 L explosion tube. A model in Simulink® has been developed to automatically analyze the videos. It is then used to estimate the flame profile, its stretching rate and convert the spatial velocity into a burning velocity by using the methodology developed by Andrews and Bradley [2] for the

Illustration: Vertical velocity versus time in a dust cloud dispersed in an explosion tube



Main results

Good agreements were obtained between particle velocities and turbulence levels measured by Particle Image Velocimetry and those determined by simulations. The relation between the initial turbulence and the homogeneity of the dust dispersion has also been assessed.

The presence of few percents of pyrolysis gases, as low as 1 %v., induces changes in the rate-limiting step of the combustion reaction, which implies a significant decrease of the minimum ignition energy and an explosivity increase. Moreover, the influences of pyrolysis gases are effective both on the combustion kinetics, but also on the flame hydrodynamics [3]. A model based on the flash pyrolysis of organic compounds has been developed and validated.

The initial turbulence of the dust cloud has a strong influence on the flame propagation. The Markstein length (i.e. effect of curvature on burning velocity) is essential for the transformation of laminar burning velocities into turbulent ones, and consequently for dust

References

- [1] Khalili et al., Powder Tech., 2011, 217.
- [2] Andrews & Bradley, Com. & Flame, 1972, 18
- [3] Dufaud et al., Ind. & Eng. Chem. Res., 2012, 90 (4)

2015



Experimental study and modeling of hybrid solid/solid explosions: an application to mixtures of graphite/metal dusts

Miriam D'Amico (2nd year)

Olivier Dufaud¹, Jean-Claude Latché²

¹LRGP, SAFE – ²IRSN



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 explosivity 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

Objectives and stakes

Even if some experimental data are available on graphite powder explosion, a parametric study of the influences of particle size distribution, humidity and initial turbulence remains to be carried out. Moreover, the potential effect of the presence of metals dusts, as magnesium or iron, on the explosion of graphite powders should be investigated. Indeed, it has already been demonstrated that hybrid solid/solid mixtures can exhibit peculiar behaviour even for low content of highly combustible dusts [2].

Methodology/ Experimental approach

Two complementary approaches have been used. On the one hand, the possibility of ignition of these mixtures has been assessed, by determining the minimum energy and the minimum temperature required to obtain a combustion phenomenon, both in dusts clouds and layers. On the other hand, the explosion severity has been quantified by measuring, in the normalized 20 litres sphere, the maximum overpressure and rate of pressure rise as a function of the metal concentration in the dust and of various parameters, such as particle size distribution, ignition delay time and ignition energy. The influence of the turbulence on the dust dispersion and the propagation flame speed have been also studied.

Illustration: 20 litres sphere for dust dispersion studies



Main results

Considering the minimum ignition temperature and energy of a dust cloud, magnesium/graphite mixtures ignite, whereas no ignition has been recorded for iron/graphite mixtures (up to 1000°C and up to 1 joule, respectively). The addition of 30% wt. of magnesium produces a decrease of 43% in temperature and 100% in energy. Even for lower weight percentages of magnesium, a considerable decrease can be observed on minimum temperature: for example, the introduction of 5% wt. results into a decrease of about 300°C. Such behavior is less marked regarding the minimum energy. Conversely, considering inflammation in layers, no ignition has been recorded for magnesium/graphite mixtures whereas greater the iron amount, easier the beginning of the oxidation process. Such metals show very different thermal diffusivities and oxide layers structures.

Synergistic effects have been clearly observed analyzing the explosion severity of such mixtures, such as the doubling of the rate of pressure rise when 15% wt. of 20 µm magnesium is introduced in the graphite dust.

All results obtained in this study will support the development of a model to compute laminar flames in dust suspension and will provide

References

- [1] Trélat S., International conference of agricultural engineering, 2012.
- [2] Dufaud O., J Loss Prevent Proc, 2012, p 853-861

2015



Experimental and computational approaches to the particles dispersion in a turbulent flow: Application to dust explosions

Carlos Murillo (3rd year)

Olivier Dufaud¹, Nathalie Bardin-Monnier²
¹LRGP, SAFE



General context, scientific issues

The experimental determination of the *flammability parameters* of a combustible dust implies significant variations of factors that require several attempts to establish its ignitability properly. The modified Hartmann tube is a standard test widely used to determine the flammability characteristics of combustible dust. Moreover, the uncertainty level of this test varies according to the physical properties of the analyzed material and the conditions defined for the experiments.

Objectives and stakes

The aim of this work is to determine the influence of operating parameters such as the dispersion pressure, the ignition delay and height on the dust flammability.

For this purpose, the particles dispersion within the dust cloud of the standardized flammability tests has been analyzed by describing the evolution of the turbulent two-phase flow associated to the dust cloud.

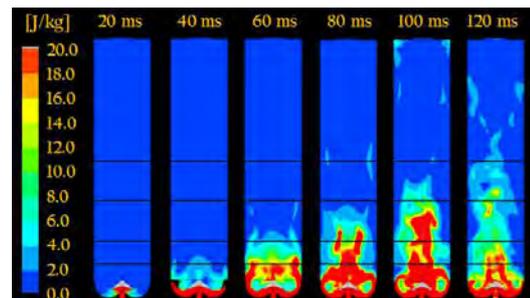
Methodology/ Experimental approach

An experimental approach determined the parameters that influence the conditions of the dust/air mixture. The dispersion of the dust were characterized by granulometric analyses. Moreover, a Computational Fluid Dynamics (CFD) simulation, based on an Euler-Lagrange approach, was developed and validated with the results obtained with the experimental approach.

The case study that was considered for this study is micrometric wheat starch. This is a combustible dust that is submitted to the fragmentation and agglomeration phenomena due to its cohesive behavior.

Illustration:

Evolution of the turbulent kinetic energy in the modified Hartmann tube



Main results

The analysis of the influence of the main operating parameters of the modified Hartmann tube is an important tool to study the variability of the flammability parameters of a combustible dust. A preliminary characterization of the dispersion mechanisms inside the vessel, by using CFD tools for instance, might constitute an insight for defining the most conservative conditions for an experimental procedure.

In the peculiar case of starch/air mixtures, the results show that an ignition performed between 80 and 120 ms with an injection performed at 5 bars is appropriate for an acquisition of the flammability data and to improve the experimental reproducibility. Ignition tests confirm this statement. Additionally, the results suggest that the location of the ignition sources should be of approximately 10 cm over the dispersion nozzle in order to have a relatively low turbulence level during the dust ignition. These characteristics pose the importance of the analyses of the physical properties of the gas and the dust in the description of the two-phase flow and its effects on the experimental results.

References

[1] Di Sarli, (2014). CFD simulations of dust dispersion in the 20 L vessel: Effect of nominal dust concentration. *Journal of Loss Prevention in the Process Industries*, 27: 8-12.

2015



INFLUENCE OF MOISTURE ON THE PRESSURE DROP OF NANOSTRUCTURED DEPOSIT

Ribeyre, Quentin (2011-2015)

D. Thomas, A. Charvet, C. Vallières
LRGP, SAFE



General context, scientific issues

Air quality has emerged as a major public environmental/health issue. Almost all fine particles in the air are manufactured and there are many questions regarding the impact of these ultrafine (<100nm) particles on human health. Thus, to protect workers, institutions use particulate air filters placed within the flow of general ventilation. Almost all of the data available on the temporal evolution of filter pressure drop corresponds to standard ambient air conditions. Despite this, few studies focus on the interaction of water moisture on the deposit formed by these nanoparticles and the impact on the pressure drop.

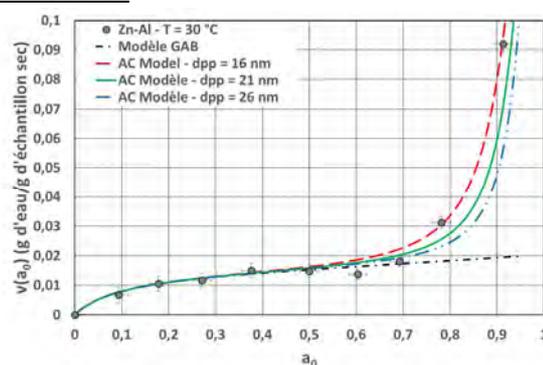
Objectives and stakes

- Development of an adsorption-condensation model (applicable to nanoparticles).
- Measurement and modelling of the pressure drop changes of nanostructured deposits under humidity.

Methodology/Experimental approach

The first part of this study consists of the measurement of sorption isotherms of four nanostructured powders. A semi-predictive sorption model based on the theory of the multimolecular adsorption (GAB equation) and on the capillary condensation (Kelvin's law) was developed. The second part of the study describes the thickness and pressure drop variations of a deposit formed by these nanostructured particles for different values of humidity. Through the thickness variation of the media and adsorption-condensation model, the porosity for each humidity value has been calculated. Following this, three pressure drop models available in the literature have been modified by introducing cake thickness and porosity variation according to relative humidity. Finally, a rheological analysis of powders is proposed to quantify the cohesion changes under moisture conditions.

Illustration



Comparison of experimental and modelled water sorption isotherm (example of Zn-Al powder).

Main results

- Good agreement between Adsorption-Condensation model (AC model) and experimental sorption isotherms for all the nanostructured samples.
- Development of an experimental setup to describe the pressure drop variations of nanostructured filtration deposits.
- Implementation of the AC model in three pressure drop models available in the literature (described by Kozeny-Carman, Mauret-Renaud and Thomas) to predict the pressure drop evolution of a nanostructured deposit at various humidities. These models have been modified by introducing cake thickness (experimentally measured) and porosity variation (calculated) according to relative humidity.
- Good agreement between experimental and modelled pressure drop evolution.
- Highlighting, thanks to a rheological analysis, of changes of deposit cohesion under moisture conditions (viscosity and critical shear stress increase).

References

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- Q. Ribeyre et al (2015) *Influence de l'humidité de l'air sur la perte de charge d'un dépôt de particules ultrafines ou nanostructurées*. Récents Progrès en Génie des Procédés 107.



Development of new synthetic fibrous media based on submicron fiber: application to aerosol filtration

Selven Rungiah (2nd year)

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1. LRGP – SAFE – 2. Gemtex



General context, scientific issues

Nonwoven filter media are widely used in filtration applications [1]. In air filtration, one of the main objectives is to have the best efficiency for the smallest pressure drop. According to Podgorski et al. (2006) and Wang et al. (2007) [2,3], using submicron fibers increases the ratio between efficiency and pressure drop ("quality factor") so submicron fiber media have high efficiency with a relative low pressure drop. Graham et al. (2002) [4] reported the low pressure drop is due to the modification of the air flow by the presence of submicron fibers generating a slip flow effect. Nowadays, the main technologies that could perform submicronic fiber-based structures are the electrospinning, the nano-meltblown, and the bicomponent island-in-the-sea spunbond technologies [1-2].

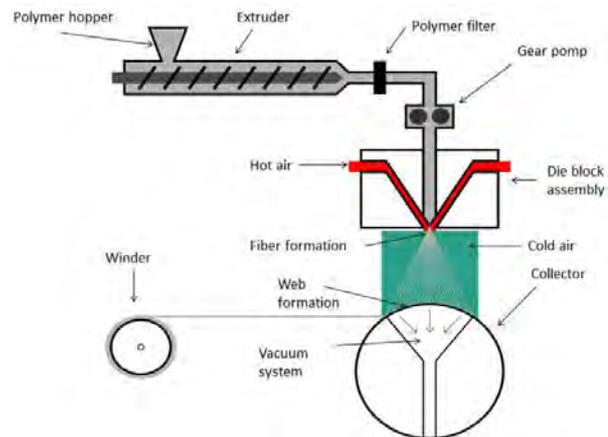
Objectives and stakes

This work is a part of the FUI Filairco consortium. The aim of the thesis is to develop submicron fiber media structure based on two methods with high productivity rate compare to electrospinning: nano-meltblown process and the bicomponent island-in-the-sea spunbond technologies and then show how submicron fibers impact the filtration performance (efficiency and permeability).

Methodology/ Experimental approach

The methodology consists of two parts: First, the two technologies for creating submicron fibers are analysed in depth in order to understand the relationship between the process factors and the structural parameters (fiber diameter, packing density, basis weight, thickness...) with experimental design and statistical analysis. Then, the relations between filtration properties and the structural parameters are investigated. The permeability is measured with a flowmeter from 0 to 200 l/min and the collection efficiency is measured with NaCl particles with a filtration bench test. The filtration analysis is completed by the development of filtration model.

Illustration: Nano-meltblown process to produce submicron fiber



Main results

The first analysis of the two processes draws a global overview of the relationships between process factor and structure. For instance, in the case of nano-meltblown: polymer throughput and pressure air impact the fiber diameter. And in the case of the bicomponent island-in-the-sea spunbond technologies: the polymer ratio island/sea is one of the main factors on the fiber diameter. For optimizing the process parameters according to the first results, a large range of structures is developed (submicron to micron fibers...) and tested in filtration. Some fiber media tested have lower collection efficiency compare to theoretical model prediction. One cause could be the heterogeneity like the non-uniform packing density or the fiber size distribution which affected the air flow. Future works will aim to (i) complete the study of relationship parameter process/structure to create submicron fiber and (ii) complete the filtration test performance and develop a filtration model incorporated the heterogeneity of the structure.

References

- [1] Payen et al, .SallesPropres, 60, 65–72.
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- [3] Podgorski et al. Chemical Engineering Science, 2006, 61, pp 6804-6818.
- [4] Graham et al. Fifteenth Annual Technical Conference & Expo of the American Filtration & Separations Society. 2002.

2015



Alternative process for the cleaning of blast furnace fumes

Guillemette THIEFFRY (2nd year)

Augustin CHARVET, Nathalie BARDIN MONNIER, Dominique THOMAS
LRGP, SAFE



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 freed from particles or at least with a very low dust content.

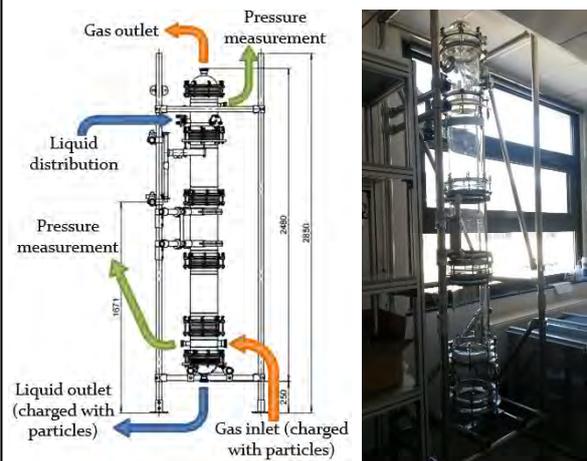
Objectives and stakes

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 in order to decrease particle concentration. With that objective in mind, a new filtration process has been developed in order to treat high flow rates with a good collection efficiency and a limited and constant pressure drop.

Methodology/ Experimental approach

The chosen technology is a wet granular bed i.e. a combination between a traditional granular bed and an absorption column, in which the gases are filtered through a collectors stack and the particles collected are continuously re-entrain thanks to a water film flow. The main difficulty in the design of the separator is the selection of the operating parameters (air and liquid flow rates) and the characteristics (collector diameter) which permit to obtain a good efficiency (close to a filter media efficiency) while maintaining a constant and limited pressure drop.

Illustration: Filtration column



Main results

Unlike a traditional granular bed, there is no correlation for determining the theoretical pressure drop and collection efficiency of a wet granular bed. A program was realized with the software Matlab® to estimate the initial theoretical efficiency and pressure drop of a traditional granular bed. It enabled us to design the pilot which will be used for the tests. It consists of a glass column with a diameter of 20 cm and a length of almost 3 m. The gas will be filtered through glass beads with a flow rate between 10 and 20 m³ h⁻¹ and the water flow rate will range between 0 and 2 m³ h⁻¹.

First experiments will be done with the wet granular bed to measure the initial collection efficiency and pressure drop and to compare them with a dry granular bed. Then, experiments will be performed to select the ratio between air and liquid flow rates in order to reach the best "unclogging" of the granular bed.

References

[1] IEA, 2007. Tracking Industrial Energy Efficiency and CO₂ Emissions.

<p>2015</p> 	<p>Effects of Nanoparticles Insertion on Gas Mixtures Explosions</p> <p>Torrado, David (1st Year)</p> <p>Olivier Dufaud¹, Pierre-Alexandre Glaude² ¹SAFE, ²KinCom</p>	
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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 the industries (mainly coal mines and power generation plants). Recent studies of the explosible characteristics of these system have been conducted, however, there is a limited information regarding the combustible nanopowders/gases mixtures. This project focuses in carbon black's 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 or 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's sphere is used in order to determine the maximum overpressure and rate of pressure rise as a function of the nanoparticles concentration, the gas molar fraction and the initial system's turbulence. The combustion gases are analyzed in a micro-chromatograph. The flame velocity is measured in a vertical 1 m long tube with a square cross-section of 0.07 m connected to a gas mixing system. 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.

Illustration



Main results

The maximum overpressure and the rate of pressure rise has been measured for methane/air and propane/air mixtures and taken as reference values. The results shows that these explosion's parameters rise until the stoichiometric concentration and then a decrease is observed with the augmentation of gas concentration. The maximum pressure did not change significantly with the initial turbulence of the mixture, nevertheless, the rate of pressure rise is considerably higher when the initial turbulence is incremented. It is expected that the insertion of carbon black nanopowder on the mixture will produce lower values of the rate of pressure rise and the maximum overpressure. This behavior could be explained assuming that the nanoparticles of carbon black is a soot cloud which improve the physical and chemical condensation of combustion products. The front flame propagation video of carbon black dispersion on a methane/gas mixture the powder dispersion changes the thermic heat transfer, notably the radiation heat exchange.

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2015



Adsorption on activated carbon applied in gas mask respirator cartridge: exposure to organic vapours mixture

François Vuong (2nd year)

Cécile Vallières
SAFE



General context, scientific issues

Respirator cartridge is widely used to protect operators exposed to toxic vapours. Whereas anti-gas cartridge filters are classified following standards (NF EN 14387+A1), which are based on breakthrough time requirements at several types of reference vapours exposure, the presence of a vapours mixture is more realistic. This is a crucial issue because breakthrough times can be reduced and breakthrough concentration can exceed the exposure concentration [1]. This gives insight for safety standards actors to draw suitable guidelines to protect more effectively gas mask users.

Objectives and stakes

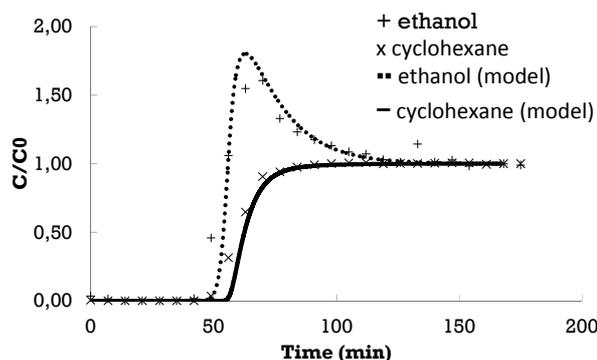
Respirator cartridge is able to remove pollutants from the air by adsorption on activated carbon. A first model [2] was built to describe the adsorption of single vapour. This model was extended to predict the breakthrough of binary vapour mixture using only kinetics and equilibria from single vapour adsorption.

Methodology/ Experimental approach

The experimental setup consists of a column filled with commercial activated carbon, exposed to a mixture of organic solvent diluted in a constant nitrogen gas flow.

A gas chromatography coupled with a FID detector permits to monitor the gas composition at the end of the column. A breakthrough curve is then obtained, in which apparent diffusivities and uptakes of each components are measured. The results will be compared to our dynamic bed adsorption model assuming the Extended Langmuir equilibrium and using a modified expression of Linear Driving Force (LDF) coefficient to describe mass transfer in the column. This coefficient is only function of single adsorption kinetics data and the gas composition.

Illustration: Breakthrough of the column exposed to ethanol (1000ppm) and cyclohexane (4000ppm) vapours in mixture.



Main results

Breakthrough curves were also obtained using acetone/ethanol and cyclohexane/heptane vapours mixtures. In the present graph, a roll-up is noticed, which is attributed to a concentration exceeding the exposure concentration due to affinity difference between species.

It was first assumed a LDF hypothesis to describe the mass transfer equation. The associated coefficient for both compounds must be function of the mixture composition. Letting the coefficient of each species equal to that obtained in single adsorption, leads to satisfactory results in a safety point of view. The binary adsorption predictive model was able to match all breakthrough times with an error inferior to 15%.

Further works will focus on the mass transfer in activated carbon for binary mixture, and its modelling by a Maxwell Stefan approach [3]. It will take into account the mutual effect of covapors in the expression of the mass transfer coefficient. This simple expression will also distinguish the diffusion part from the counter diffusion part of the column.

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2015

Metallic ultra-fine particles granular bed separation



Loic Wingert^{1,2} (2nd year)

Denis Bémer¹, Augustin Charvet², Nathalie Bardin-Monnier²,
Dominique Thomas²
¹INRS, ²LRGP (SAFE)



General context, scientific issues

Ultrafine particles are generated by many manufacturing processes such as surface processing and coating etc... The most efficient and widely used de-dusting methods for separating the particles from the carrier fluid are currently fibrous media which have to be frequently replaced because of a irreversible clogging. As an alternative, granular beds exhibit interesting performance, in terms of ultrafine particles collection efficiency and operation time by exploiting a greater depth. Furthermore, the unclogging might be easier especially by means of vibrations (Bémer et al., 2013).

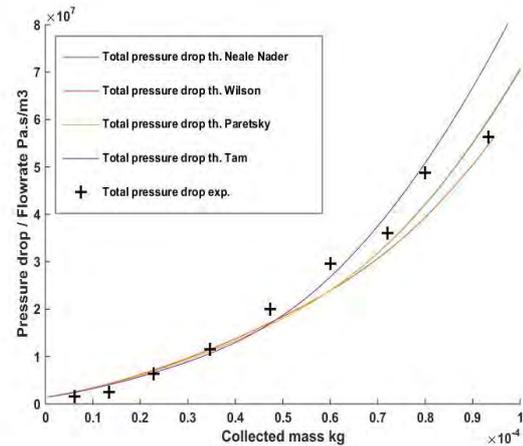
Objectives and stakes

In the case of industrial ultrafine particles filtration by a granular bed, the prediction of the efficiency and the pressure drop evolution is a key step towards the installation sizing. The existing phenomenological models of pressure drop and efficiency evolution are currently non-predictive because of the imperative knowledge of empirical values. To overcome this issue, a predictive clogging model has to be established.

Methodology/ Experimental approach

The development of our predictive model is based on several approaches. We conduct microscopic observations of the evolution of the nanoparticles deposit structure during the clogging. This should permit to correlate the changes in collector geometry with changes in pressure drop and efficiency. To validate the model, we also perform experiments to follow the clogging evolution of several granular beds by many types of ultra-fine particles. These experimental data are also used to validate a computational fluid dynamic code (Geodict®). The simulation results should be used to test our model without conducting other tedious experiments.

Illustration: Pressure drop prediction of our model



Main results

A predictive clogging model based on the expression of a collector specific area equivalent diameter was established. This latter depends on the mass of collected particles and corresponds to the clean collector diameter with the same specific area as a collector within a clogged granular bed. This approach permits to use the initial efficiency and pressure drop models to forecast the behavior of a granular media during the deep bed filtration phase. Clogging experiments of different granular beds (beads diameter of 0.5 mm and 1 mm) were conducted using ultrafine particles generated by thermal spraying. These experimental data and the model results show a very close agreement. This experimental data also permit to develop an improvement principle of the performance of the granular bed filtration by using several beads diameters in the same granular bed. This especially reduces the pressure drop increase. By comparison of the experimental results with some theoretical models, we also validate the Geodict code for predicting the initial efficiency and pressure drop.

References

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2015



Characterization of the dissemination of substances in a lentic aquatic environment

Assaad Aziz (chercheur CDD)

M-N. Pons, J-P. Leclerc
Sols & Eaux



General context, scientific issues

In the BioCapTech project, several partners have joined forces to find an ecological solution to fight against algal blooms (cyanobacteria) and herbaceous (macrophytes) in ponds. This association was conducted as part of a call for project of the Economic Mobilization Agency of the Lorraine region and the final goal is to develop an eco-sustainable treatment process of aquatic pollution. This solution requires the use of allelopathic natural substances to be dispersed effectively in the water body. The evaluation of the application and the efficiency of this solution require having a model to predict rapidly the location of treatment points and their number. This model will then be included in a decision support system for selecting the most appropriate treatment.

This model, developed by FA Moussoh must be validated first on a laboratory pilot.

Objectives and stakes

- To realize a complete experimental program, with tracking saline and fluorescent tracers which represent the natural substances used in the treatment.
- To analyse the results obtained and to compare them with the results of the numerical model.

Pilot structure

The studied pond (figure1) has a parallelepiped shape with the dimensions of 1.55 m * 0.7 m * 0.8 m. The working volume (0.4606 m³) is 1.4 m long, 0.7 m wide and 0.47 m deep. The pond is fed at a flow rate of 1 m³/h.. The inlet Reynolds number is 7300. The Reynolds number inside the pilot varies between 100 and 7 300. This large variation of the flow regimes inside the volume (laminar, transition and turbulent flow) makes that simulation of flow behavior using CFD is not straightforward despite the apparent simplicity of the system.

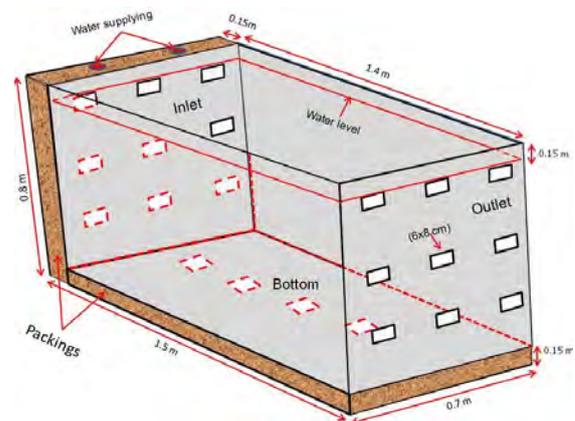


Figure1: Pilot structure which is used to validate the numerical model.

Main results

Chloride sodium was detected with very small lab-made conductimeter probes and rhodamine was measured with a submersible spectrofluorimeter (Cyclops-7TM Submersible Sensors). Numerical simulations were carried out by F.A. Moussoh using the commercial code Fluent using two turbulence models (RNG k- ϵ and SST k- ω transition turbulence models).

Figure 2 shows an example of a comparison of numerical and experimental RTD curves. The numerical and the experimental RTD measurements showed the same flow behaviors which validate the CFD simulation.

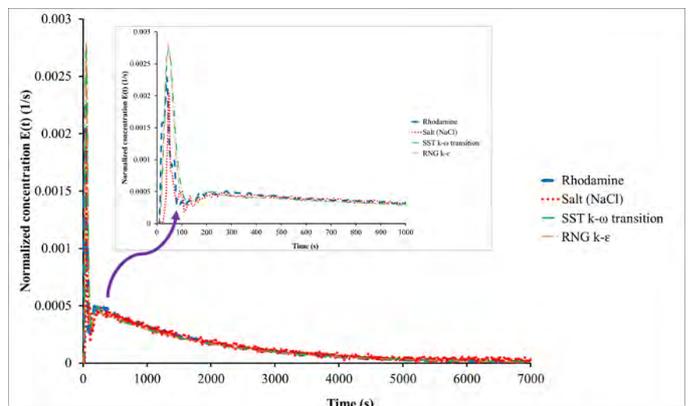


Figure2: Comparison of experimental and numerical RTD

2015



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

Nelly Chrystelle ATINKPAHOUN (1st year)

Marie-Noelle PONS, Jean-Pierre Leclerc



General context, scientific issues

Water is essential to the survival and well-being of man and is essential to the functioning of many sectors of the economy (UN, 2006). To satisfy these different needs, the population exert enormous pressures on the water resource. Therefore, many pollutants (organic matter, nutrients, micro-pollutants) are found in the water. The untreated wastewater discharged into rivers are one of the most important forms of the water pollution worldwide. The problem is even more serious in developing countries, where over 90 % of sewage and 70 % of untreated industrial waste are discharged into surface waters (UN, UNEP, FAO, 2010). This poses risks to human health and the environment. In developed countries urbanization growing, climate change and water stress will imply also changes of paradigms in wastewater treatment (reclaimed water reuse, resource recovery).

Nancy versus Cotonou (by Google Earth)



Objectives and stakes

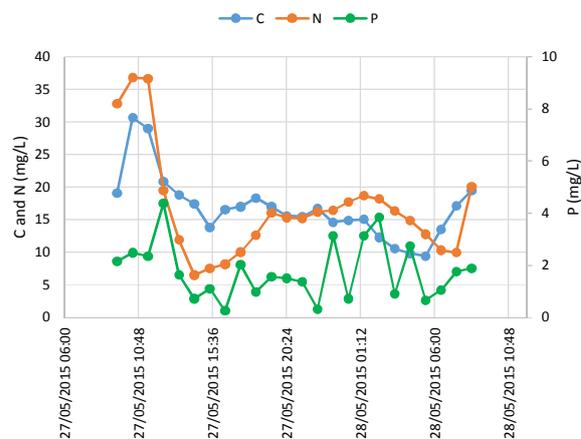
Selection and design of wastewater treatment solution implies to understand the relationships between actual (and future) socio-economical activities and pollution (in terms of macro and micropollutants) discharge.

These relationships can be summarized in models, linkable to dynamic models of wastewater treatment plants, such as the Benchmark Simulation Model n° 2 (Jeppsson et al., 2013).

Main results

The aim of the five first months of the thesis was to study the international literature related the the topic, to compare the data availability and to adjust the sampling procedures and the analytical methods between Benin and France.

The next figure shows an example of variability of C, N and P at the inlet of Greater Nancy wastewater treatment plant.



Methodology/ Experimental approach

The methodological approach consists of :

- Selection of two watersheds (one in France (i.e. Greater Nancy) and one in Benin (Cotonou))
- Collection of information on population (age distribution, daily/weekly activity, sanitation etc.)
- Selection of pollution parameters and of their analytical methods in function of lab facilities availability. In terms of micropollution, metals will be more specifically studied in a first phase.
- Sampling campaigns and samples analysis
- Wastewater generation model improvement. parameter estimation land

References

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2015



Production of nickel salts from hyperaccumulator plants at the pilot scale

Florent FERRARI (CDD)

Marie-Odile SIMONNOT, Baptiste LAUBIE
Processes for Environment, Safety and Resource Recycling



General context, scientific issues

Huge areas in the world are covered by soils containing high metal contents. Agromining aims at recovering these metals by growing hyperaccumulator plants and treating the metal-rich biomass by pyro or hydrometallurgical processes. *Alyssum murale* is a plant able to reach high Ni yields : 100 kg Ni per ha. Once harvested and dried, *A. murale* biomass is incinerated and the ashes are treated by a hydrometallurgical process that we have designed to produce high value added salt. This process has to be up-scaled to the pilot scale in order to launch a start-up project to develop this activity. This work is granted by BPI France (maturation project).

Objectives and stakes

- Produce nickel salts at the pilot scale.
- Evaluate the feasibility of a start-up

Methodology/ Experimental approach

Starting from the process developed to produce ammonium nickel sulfate hexahydrated salt (ANSH) from *A. murale* ashes (Barbaroux et al., 2012; Zhang, 2014), a new protocol has been established to synthesize a chemical intermediate of a nickel salt range. A biomass-fired boiler has been purchase and a pilot including 2L, 5L and 10L jacketed glass reactors has been designed. The new process has been tested on the pilot and all procedure steps of have been controlled by ICP-AES analyses.

Illustration:



Main results

- From former ANSH process, 2 Kg $\text{ANSH} \cdot \text{week}^{-1}$ can be produced with an ANSH/ashes yield of $0,83 \text{ Kg ANSH} \cdot \text{Kg ashes}^{-1}$.
- Our results have demonstrated the feasibility of a synthesis of the chemical intermediate at the pilot scale with a purity of 95%.
- This chemical intermediate allows the synthesis of at least 5 new nickel salts.
- A bibliometric analysis is ongoing to identify the potential commercial of each nickel salt.

References

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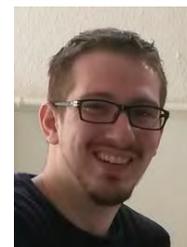
2015



Generalization of the compartmental approach for reactor modelling using tracer experiments data and CFD simulations.

HAAG, Jérémie (Year of PhD : 2)

LECLERC Jean-Pierre, Cécile Lemaitre, Caroline Gentric



General context, scientific issues

Modelling of chemical reactors is often based on two different approaches: (a) a network of elementary reactors taking into account heat and mass transfer and chemical reactions (b) Reactive Computational Fluid Dynamics. The first method is simple but gives a poor representation of the physical processes. The second method is robust but complex to conduct. Recently an intermediate approach called “compartmental modelling” based on the description of the reactor by a complex network of elementary cells derived from tracer experiments, technical information about the studied process and non CFD simulation was developed for some examples.

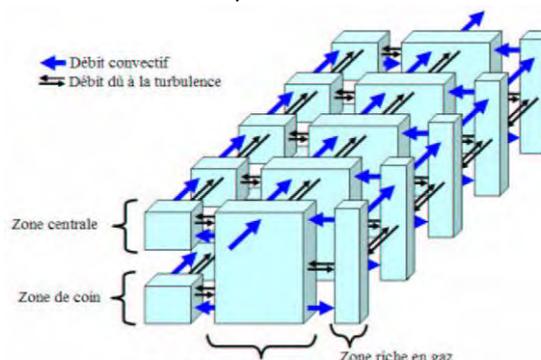
Objectives and stakes

- To develop a general methodology for rapid, simple and physical meaningful of chemical reactor.
- To develop the corresponding software and to validate the methodology on several examples.

Methodology/ Experimental approach

Use of Tracer experiments to recover information about the flow behavior.
Division of the reactor in a network of elementary volume based on calculated data (velocity, turbulence, gas fraction...).
Determination of a network of interconnected elementary cells and estimation of convective and turbulence exchange rates.
Numerical RTD of the proposed network.
Simulation of the reactor performance by taking into account chemical reactions.

Illustration Typical example of compartmental modeling applied to a biological reactor (Le Moullec et al. 2010)



Main results

- State of art on the existing modelling approaches and theoretical set-up of the general methodology.
- Development of tracer experiment data processing software. Graphical interface realized by PROGEPI
- Development of a routine in FORTRAN language able to simulate the RTD of any complex 3D network of perfect mixing cells. Coupling of chemical reaction is under development.

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2015



Hybrid Geomaterials and Photocatalysis: An Efficient Procedure for Depollution of Water

Hawraa Ayoub

(1st year)

Thibault Roques-Carmes, Olivier Potier



General context, scientific issues

In the aquatic environment, pharmaceutical active compounds (PPs) have been recognized to be a group of emerging environmental contaminants. Their occurrence in the aquatic environment has been recently investigated and it is principally due to insufficient removal in wastewater treatment plants (WWTPs) [1]. Consequently, variable quantities of pharmaceuticals can reach surface waters, groundwaters, and sediments, resulting in concentrations ranging from nanograms to micrograms per liter. Even at very low environmental concentrations, they have a negative effect on non-target organisms [2].

Objectives and stakes

For most pharmaceutical contaminants, the setting up of an analytical protocol is an on-going process, with validated methods unstandardized. The aim of this study is to develop an efficient analytical procedure, that allows the quantification of pharmaceutical contaminants such as diclofenac, at the ng/L level in contaminated rivers, and compare their distribution in France and other countries as Germany. Then we will synthesize an efficient catalyst for the removal of the contaminants by photocatalytic degradation [1].

Methodology/ Experimental approach

Our work starts with samplings and detection procedures. Since we are dealing with micropollutants, the need for preconcentration method is very important for the detection. This will be done by using solid phase extraction technique. It will be followed by a series of analytical detection analysis mainly HPLC. Then we will synthesize a geomaterial catalyst after finding the appropriate composition that gives an efficient photocatalytic removal. Zeolite corresponds to one of the catalyst components used such as ZSM-5 zeolite.

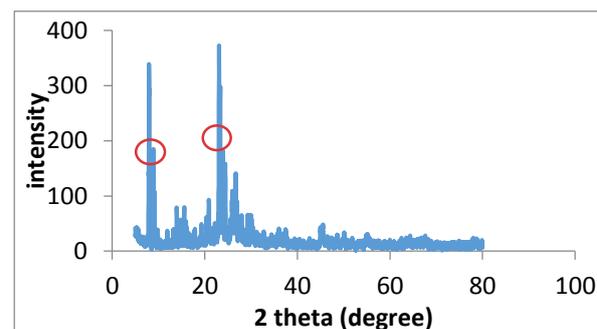
Illustration

Synthesis of ZSM-5 zeolite for catalyst preparation



Main results

➤ We start our work by synthesizing ZSM-5 zeolite, a template free zeolite. X-ray diffraction analysis was done to verify the formation of the desired product. The XRD pattern shows peaks similar to the specific peaks of ZSM-5 zeolite mentioned in literature [3]: one at $2\theta=7-9^\circ$ and another at $2\theta=23-25^\circ$.



➤ A formation for solid phase extraction machine was done. We learned how to use the machine and we tried to analyze 3 samples: river water, distilled water and drinking water to see how the work goes on to be ready for our analysis.

References

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<p>2015</p> 	<p align="center"><u>Metals recovery presents in hyperaccumulators plants biomass</u></p> <p align="center">Hazotte, Claire (post-doc, 2015)</p> <p align="center">M.O. Simonnot, B. Laubie</p> <p align="center">Processes for Environment, Safety and Resource Recycling</p>	
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General context, scientific issues

Cadmium in soils is generally present at very low concentrations but it is a very toxic heavy metal. It is considered as fairly mobile and easily bioavailable, so it can enter into the food chain through plant uptake and also contaminate groundwater. Soil remediation is therefore a major concern. Cadmium can be extracted by different hyper-accumulator plants. The present contribution, part of the LORVER project, focuses on Cd recovery from those plants, in order to recycle this metal and avoid dumping of contaminated biomass.

Illustration

The *Noccaea caerulescens* plants were grown on the site of Sita group (Jeandelaincourt-54)



Noccaea caerulescens

- Objectives and stakes**
- Biomass characterization.
 - Process design for Cd and Zn recovery
 - Manufacturing cadmium or zinc salts
 - Economic evaluation of the process

- Main results**
- A bibliographic research has been done on metal recovery from hyperaccumulator plants and on the use of Cd and Zn for industrial purposes.
 - The first experiments of cementation were performed with a synthetic solution of cadmium (Cd²⁺) and zinc (Zn²⁺) ions. Zinc powder was added in stoichiometric proportion with the cadmium present in the solution. Results show that is possible to recover 70- 90 % of cadmium.
 - The first experiments run with the ashes of dry biomass enabled us to remove potassium by rinsing with water and transfer metals into solution by acid leaching.
 - Experiments are ongoing to recover Cd and Zn.

Methodology/ Experimental approach

The hyperaccumulators plants, *Noccaea caerulescens*, were provided by the Laboratory Soils and Environment, in the context of LORVER.

First, biomass composition of those plants was determined by ICP-AES after mineralization. It contained between 3000 to 4000 mg.kg⁻¹ dry matter. The plants also contain other metals such as Zn, Al, Cu, Fe, K, Mg and also P and S.

The first objective was to separate Cd from the other metallic elements. Experiments of calcination were run to determine the limit temperature to avoid volatilization of Cd and/or Zn and concentrate the metals in the ash. Then, biomass was leached with acid. Cementation can be a technique of hydrometallurgy used for the separation. It consists to add powder metal zinc for the reduction of cadmium:

$$\text{Cd}^{2+} + \text{Zn}^0 \rightarrow \text{Cd}^0 + \text{Zn}^{2+}$$

Reference

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2015



Innovative production of monoclonal antibodies with sequential multicolumn chromatography

Hilbold, Nicolas-Julian (1st year of PhD)

Supervisor: Laurence Muhr - Team SOLEO



General context, scientific issues

With 35% volume of marketed therapeutic proteins, monoclonal antibodies (mAbs) are today part 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, traditionally operated in batch mode. Chromatography remains the main workhorse of mAbs purification, with typically 2-4 chromatography steps^[2]. Operating chromatography in batch mode usually implies a sub-utilization of resins resulting in low productivity, 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

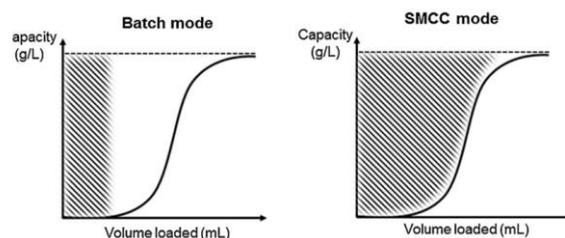
Gain knowledge on the SMCC process and continuous chromatography in general by:

- Characterizing batch chromatography system
- Using a modelling 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.

Illustration: Breakthrough curves for a bind & elute chromatography step, illustrating the difference in resin utilization between for batch chromatography and SMCC.



(see Girard et al for more details)

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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- [4] Girard, V. et al, *J. Biotechnol.* In press, (2015).

2015



Presence and fate of micropollutants in anaerobic digestion of agricultural residues

Billy Homeky (4th year)

Olivier Potier, Nouceiba Adouani
Sols et Eaux



General context, scientific issues

The thesis is part of a project, which aims to make an experimental farm self-sufficient energy using an anaerobic digester of 400 m³. During the last decade, anaerobic digestion has gained more interest as it is a way to provide renewable energy in the form of methane-rich biogas [1]. The process consists in the conversion of organic material by microbial routes. However, the veterinary monitoring of the cattle leads to the presence of antibiotics in the manure [2]. The impacts of antibiotics on biological processes are well studied for wastewater, but a little is known about anaerobic digestion of cow manure which is a complex matrix. Understanding the antibiotics' effects is therefore required to improve the monitoring of anaerobic digester.

Objectives and stakes

A first goal is the optimization of the process, so that most residues on the farm can be simultaneously converted into energy. This means the determination of the right operating conditions.

A second goal is to assess whether the presence of antibiotics impact the conversion process or not, and the inhibiting concentrations.

Ultimately, the results will serve to update the ADM1 model of the IWA by considering the impact of the antibiotics.

Methodology/ Experimental approach

For the process optimization, anaerobic co-digestion of the different residues has been investigated, and we determine the operating conditions that ensure the effectiveness of the process. Batch tests (1L) have been done where cow manure was mixed with grass silage or with lactoserum.

For determining antibiotics impacts, tests have been done in both batch (1L) and continuous reactors (4L) with increasing antibiotics concentration. The antibiotics tested are tetracycline, spiramycin and tylosin.

Illustration: Batch reactors of 1L (Left); Continuous reactor of 4L (Right)



Main results

For the anaerobic co-digestion of cow manure (100g) with grass silage (20g), several silage durations have been tested and showed that a silage time between 8 and 36 weeks improves the process. Co-digesting the manure with lactoserum (at 0.5 g/L and 2g/L of lactose) led to a slight improvement of 6% for both concentrations. The simultaneous co-digestion of the three residues (manure, grass silage with 36 weeks silage duration and lactoserum) showed an improvement of 14% when using 0.5g/L of lactose, comparatively to the control (manure only). But for 2g/L of lactose, there was a decrease of 11% in the methane production.

The assessment of antibiotics impact in batch conditions showed an inhibition of 22% for 8mg/L of tetracycline, whereas 80 mg/L and 160 mg/L showed a similar inhibition of 41%. Spiramycin showed inhibitions of 37% and 34% for 7 mg/L and 70 mg/L respectively. Tylosin led to an inhibition of 31% for 10 mg/L and 45% for 500 mg/L.

The tests in the continuous reactor showed that 20 mg/L of tetracycline inhibited the process which recovered after one week. But at 200mg/L of tetracycline, a recovery was not noticeable in one week. In the case of spiramycin, 1.4 mg/L and 14 mg/L inhibited the process which recovered after one week, but at 140 mg/L no recovery was noticed during two weeks.

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2015



Phytomining : from a lab scaled synthesis to a medium pilot scaled process.

Vivian Houzelot (Post-Doctoral fellowship)

Marie-Odile SIMONNOT^a; Jean-Louis MOREL^b
^a LRGP – ^b LSE

General context, scientific issues

Soils and wastes with high metal content are sources of compounds of industrial interest. But metal concentrations are generally too low for conventional pyrometallurgical recovery. Phytomining offers a great interest: based on the properties of some plants, named hyperaccumulators [1], that accumulate metals dispersed in soils. Thanks an innovating hydrometallurgical process developed in a lab partnership context [2,3], metals are recovered and valorized by synthesizing high value metal salts. But no works have been done and no medium scaled pilots have been built so far to attest the feasibility in an industrial context

Objectives and stakes

The objectives of this work are numerous. They consist into up-scaling the process, improving and modelizing all the steps, studying and attesting its industrial scaled feasibility and its profitability by constructing a medium scaled pilot. The pilot must be adaptable to produce different amount of one specific metal salts but also to adapt the process for different kind of metal salts.

Methodology/ Experimental approach

The first task consisted into constructing the unit by framing up all the parts that are necessary for the washing step, and the lixiviation step, and the crystallization.

The unit was tested, step by step, by following the kinetic rates and the concentration in the bulk of each chemical element. These experimental parts allowed us to write local and global mass balance to understand what the critical points in this process are in terms of yield and purity. It also allowed us to establish kinetic and economical models.

ICP-AES and TOC analysis were performed to measure the chemical concentrations in liquids and solids (after mineralization steps).

Illustrations: Picture of the 10L batch pilot built in this work



Figure 1 The hyperaccumulator *Alyssum murale*



Figure 2 The ANSH salt synthesized in this work



Figure 3 Picture of the 10L batch pilot built in this work

Main results

The 10 liters unit built shows an excellent ability to produce high purity ANSH salt (99%). It is also possible to synthesize different kind of metal salt and expand our production offer to different customers and specifications.

Several points have been improved to reach the desire specifications, especially in terms of selective precipitation to make easier the purification and crystallization steps.

A lot of results are on the way in terms of modelization and kinetics.

References

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2015



Experimental and numerical investigation of agricultural anaerobic digesters

Rainier Hreiz (Postdoctoral researcher)

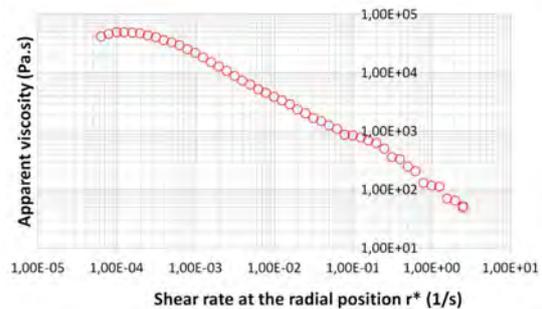
Nouceiba Adouani – Marie-Noëlle Pons
SOLEO



General context, scientific issues

Anaerobic digestion is a sustainable process for valorizing organic wastes as it produces biogas. However, predicting the process operation is challenging given the large number of involved biochemical reactions and their sensitivity to the operating temperature, the complex heat transfer phenomena with the environment, and the non-Newtonian behavior of the medium.

Illustration



Typical rheological curve of the digestate.

Objectives and stakes

This work aims at developing a model capable of predicting the long-term behavior of an agricultural anaerobic digester depending upon the composition of the feeding as well as the weather conditions (ambient temperature, wind effect, solar irradiance...).

Main results

- Rheology measurements revealed that slurry and digestate exhibit pronounced shear thinning properties and negligible yield stress.
- The viscosity values measured in this investigation were much higher than those reported in previous studies where less appropriate Couette-type rheometers were used.
- Since the digester presence leads to the heating of the surrounding soil, heat losses to the ground were found to be moderate contrary to what was supposed thus far in the literature.
- A preliminary hydrodynamic study using Fluent has revealed a poor mixing efficiency in a pilot-scale digester. The hydrodynamic modeling of the industrial-scale digester is ongoing.

Methodology/ Experimental approach

(1) Experimentally, a helical ribbon rheometer is used to characterize the rheological behaviour of the cow slurry and of the digestate (liquid phase in the digester). Such information is required so as to characterize the mixing efficiency within the bioreactor.

(2) Numerically, we are developing a model for predicting the heat transfer phenomena between the digester and the environment. This model will be coupled with the well-known ADM1 model [1] (modelling of biochemical phenomena) so as to constitute a reliable tool for simulating the long-term operation of agricultural digesters.

(3) Finally, this model will be integrated in Fluent so as to account for the effects of the non-ideal mixing on the process behaviour.

References

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2015



ION EXCHANGE (IEX) AND BIPOLAR MEMBRANE ELECTRODIALYSIS (BMED) HYBRID SEPARATION PROCESS: OPTIMAL COUPLING APPLIED TO DILUTE ORGANIC ACIDS SOLUTIONS

Meysa JAOUADI (3rd year)

MUHR Laurence, HANNACHI Ahmed (LRGP, GPSI)



General context, scientific issues

Effluents containing diluted organic acids are generated by many processes. For environmental considerations, these effluents need to be treated. The elimination of compounds such as acetic acid can also be of interest during continuous fermentation processes to limit the inhibitive effect of this acid [1]. Conventional treatment of such effluents using bipolar membrane electro dialysis is widely used for the recovery of organic acids into valuable concentrated organic streams [2]. However its limited yield and its high energy consumption are pushing towards the development of alternative hybrid processes.

Objectives and stakes

This work is dedicated to the study of a hybrid separation process for the treatment of dilute acetic acid effluents using bipolar membrane electro dialysis (BMDE) associated with ion exchange resin (IEX). Preliminary work comparing the performance of using solely BMDE and BMDE coupled with IEX showed the benefits of hybrid processes [3]. The influence of resin type and strength on acid recovery and energy consumption is investigated.

Methodology/ Experimental approach

The experimental study was carried out on a press-filter type pilot unit. The cell is composed of four compartments separated by a bipolar membrane, an anionic membrane and a second bipolar membrane. Batch treatments of 0.2% w acetic acid solutions under constant current density are conducted. Acetic acid migrates from the second to the 3rd compartment where it gets concentrated (Figure1). For each batch treatment, acetic acid concentration, conductivity, pH in weak and strong acetic acid compartments along with the voltage between electrodes are followed.

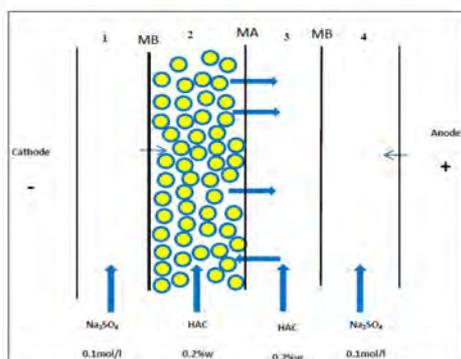


Figure 1 : Principle of the hybridizing

Illustration Typical evolution of pH and concentration in both compartments are shown in Figure 2 and 3.

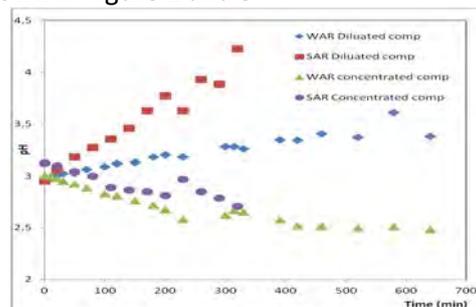


Figure 2 : Evolution of pH in both compartments (WAR: weak anionic resin, SAR: strong anionic resin)

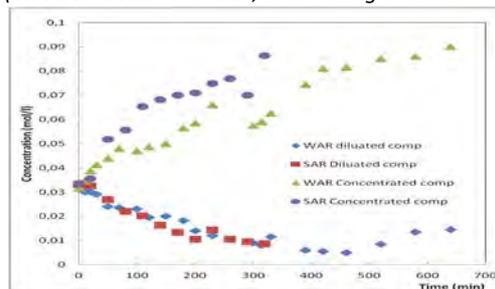


Figure 3 : Evolution of concentration in both compartments

Main results

When coupling bipolar membrane electro dialysis with ion exchange for acetic acid recovery, an optimal choice of the resins can be done. Regarding the anionic resins in the dilution compartment, the choice of a strong or weak type of resin depends on the experimental conditions and the objectives: if batch mode (adsorption/electro-regeneration) is used, weak resins may be preferable because they are easier to regenerate whereas if continuous mode (electro-deionization) is used, strong resins, which presents a higher affinity for acetate ions, may enable lower residual concentrations to be reached. The presence of strong cationic resin in H⁺ form in contact with the anionic membrane has a favorable impact on the driving force that allows acetate ions to migrate from the diluted towards the concentrated compartment.

References

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2015



Hydrometallurgical recovery of zinc, manganese and lead from pyrometallurgy sludge

Julien Mocellin (3rd year/co-supervised PhD)

G. Mercier¹, J.F. Blais¹, M.O. Simonnot², J.L. Morel³

¹INRS ETE (Canada), ²LRGP, ³LSE



General context, scientific issues

Large quantities of ferromanganese sludge are generated as waste material by blast furnace during the manufacturing of ferromanganese. These slags are very rich in manganese, zinc and lead (5 to 40 %). In the last decades, these residues have been deposited in retention ponds in periphery of the ferromanganese industry (e.g. Pompey, Lorraine region). Considering the market value of the metals, these brownfield sites can now be considered as secondary resources. We have developed a hydrometallurgical process for selectively leaching Zn, Mn and Pb in order to produce compounds of Mn and Zn pure enough to be economically recoverable and a residue rich in Pb.

Illustration



- Leaching step
- Precipitation of MnCO_3
- Precipitation of ZnS

Objectives and stakes

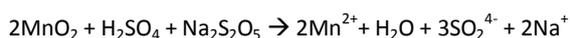
- To develop a hydrometallurgical process for the selective leaching of Zn and Mn,
- To produce pure and recoverable compounds of Zn and Mn,
- To decontaminate these industrial sites.

Main results

- Batch laboratory experiments were carried out, following experimental design, to determine appropriate leaching conditions to maximize zinc and manganese extraction. The optimum conditions for Zn extraction were as follows: temperature 20 °C, solid/liquid ratio 1:10, sulfuric acid concentration 0.25 M and three 20 min leaching steps, enabling us to extract 75% of Zn. The optimum conditions for Mn extraction from the residues were: acid concentration 0.25 M, leaching time 120 min, and a $\text{Na}_2\text{S}_2\text{O}_5/\text{Mn}$ stoichiometry of 1 to obtain 100% extraction. The leaching solution contained 754 mg/L of Zn and 10125 mg/L of Mn. It was then purified to obtain high-value precipitates of ZnS or MnCO_3 with a fairly acceptable concentration of impurities. It was therefore possible to obtain a precipitate of MnCO_3 with 45.3 % of Mn with a low concentration of impurities like Na, S, Zn and Pb. These results have been patented.

Methodology/ Experimental approach

The approach consists in selectively solubilizing Zn, obtaining a first leachate and, after solid liquid separation, Mn is solubilized from the solid already depleted in Zn. Pyrolusite (MnO_2) is stable in acidic and alkaline conditions. Extraction of Mn(IV) must be carried out under reducing conditions. Most studies have leached with sulfuric acid using a reducing agent. $\text{Na}_2\text{S}_2\text{O}_5$ will be used as a reducing agent in this process:



The leachate contains impurities and further purification of the solution is required. The purpose is to precipitate metals like Fe, Al and Si in a first step while keeping Zn and Mn in solution at chemical costs as low as possible. After solubilization of Zn and Mn, Zn is precipitated by adding Na_2S to produce ZnS and Mn as MnCO_3 by adding Na_2CO_3 . Zn could also be electrodeposited or precipitated as $\text{Zn}(\text{OH})_2$.

References

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2015



BioCapTech

CFD simulations and evaluation of dispersion of active substances for algae treatment in water bodies

Amahoué François, MOUSSOH (3rd year)

Marie-Noëlle Pons, Jean-Pierre Leclerc



General context, scientific issues

The presence of nitrates coupled to high temperature can cause eutrophication in water bodies. Eutrophication is a process of nutrient overenrichment of a water body [1], resulting in accelerated biological productivity. The state of the art regarding methods of control against plant invasions in aquatic environments has led to carry out research (such as the Biocaptech project) to find new processes. The utilization of CFD to simulate the dispersion of treatment substances in eutrophicated water bodies is an innovative contribution for the optimization of effective treatment.

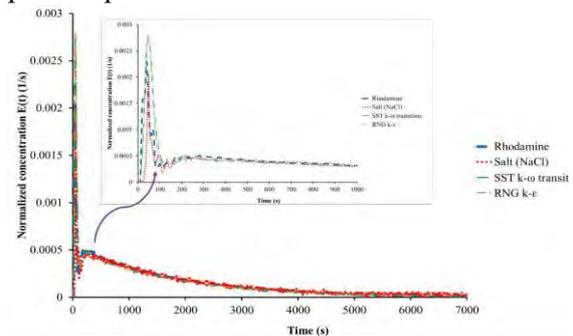
Objectives and stakes

The global objective is to develop an innovative process to locate the area to be treated and effectively target aquatic plants to treat. The treatment of these fish ponds overrun by invasive aquatic plants (algae) requires the understanding of the hydrodynamic behavior of flow through the Computational Fluid Dynamics (CFD) simulation [2]. Then, ensure an optimal treatment based on acceptable concentration of product that could kill the targeted invasive plants.

Methodology/ Experimental approach

Numerical simulations were carried out using the commercial code Fluent using five turbulence models (Sk- ϵ , RNG k- ϵ , Rk- ϵ , RSM, and Transition SST). A species transport method was used to predict numerical Residence Time Distribution (RTD). In order to validate the choice of the turbulence models, experimental RTD have been measured using two types of tracers. Chloride sodium (NaCl) was detected with very small lab-made conductimeter probes and rhodamine was measured with a submersible spectrofluorimeter (Cyclops-7TM Submersible Sensors).

Illustration: Comparison of experimental and numerical Residence Time Distribution in a fish pond at pilot scale



Main results

The contours of flow velocity magnitudes and the velocity vectors simulated with several flow rates are examined and the global hydrodynamic behavior is determined. We tested several operating conditions for the experimental tracer injections. The velocities vectors show that the flow is independent of the slope of the pond bottom. The velocity contour and vectors show that the global flow is divided into three main zones inside the pond. The above illustration shows that the numerical and the experimental RTD measurements give the same global flow behavior. However, each of the five turbulence models tested predicts differently the local hydrodynamic behavior in low flow rates areas inside the pond. The RNG k- ϵ model is finally chosen for the rest of the work. The dispersion monitoring of the simulated tracer which is injected at a position located within the pond (in a low-velocity area) shows that the choice of model affect the local dispersion.

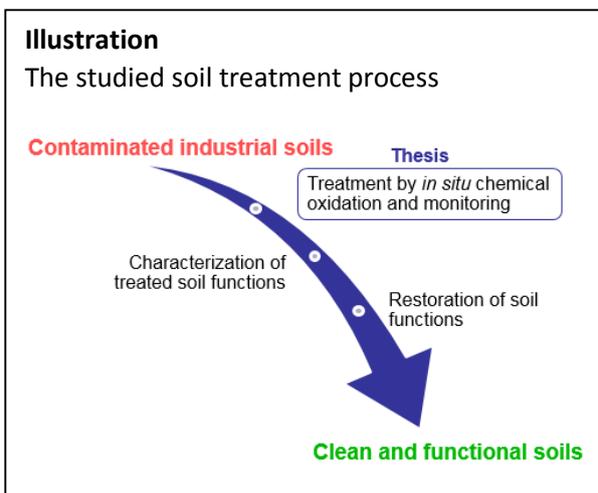
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<p>2015</p> 	<p><i>In situ</i> chemical oxidation of the unsaturated zone of former industrial soils contaminated with Polycyclic Aromatic Hydrocarbons</p> <p><u>Bérénice Ranc (2nd year)</u></p> <p>Marie-Odile Simonnot¹, Pierre Faure², Véronique Croze³</p> <p>¹ LRGP (Processes for Environment, Safety and Resource recycling) ² LIEC; ³ ICF Environnement company</p>	
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General context, scientific issues

Polycyclic aromatic hydrocarbons (PAHs) are pollutants of major concern [1]. They have a complex chemical structure and are sparingly available in the unsaturated zone of industrial soils (e.g. coking plants and MGP sites). As a consequence, specific soil clean-up techniques must be used. *In situ* chemical oxidation (ISCO) is one of these techniques and involves injecting oxidants into the soil to convert organic pollutants into less harmful chemical compounds [2].



Objectives and stakes

The thesis is a part of the Bioxyval project (AMI) and aims to assess the feasibility of the implementation of the Oxysol process in the field. Oxysol combines ISCO, soil construction and revegetation to turn a contaminated soil into a clean and functional soil.

Main results

At the end of the field implementation, the objective is to reach a concentration of the 16 parent PAHs prioritized by the United States Environmental Protection Agency below 50 mg/kg of dry soil for at least one of the combination “oxidizing solution/contact technique”. The choice of the optimal solution will be done with a consideration for environmental and economic aspects of the process. The final aim being to allow the restauration of soil functions, environmental aspects include i) the use of moderate oxidant doses and ii) the quantification and the estimation of the toxicity of the by-products resulting from the oxidation of PAHs, especially oxygenated polycyclic aromatic compounds. Economic aspects include i) a fast treatment and ii) the use of cost-effective reagents. The results should lead to specific recommendations to facilitate the implementation of ISCO for the treatment of a complex organic pollution of the unsaturated zone of soils.

Methodology/ Experimental approach

The first step is to determine the most efficient oxidizing solutions (oxidant and appropriate catalysts and/or additives) and the associated doses on lab-scale. A single oxidation not generally achieving acceptable results, a pre-treatment operation can be added in order to enhance PAH desorption and increase PAH availability. The methodology of the Design of Experiments (DOE) is used to identify the critical oxidation parameters.

The second step is the field-testing of the two best oxidizing solutions tested in the laboratory. Two new issues appear: the duration of the treatment and the contact of the oxidizing solution with pollutant. Several techniques will be implemented on the site of a former coking plant in Lorraine (France).

References

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2015



Integrative Life Cycle Assessment of biomass growth for industrial use by valorization of brownfields and wastes

Jérémy Rodrigues (2nd year)

Marie-Noëlle Pons, Marie-Odile Simonnot
Processes for Environment, Safety and Resource recycling



General context, scientific issues

Industrialized countries are facing a triple challenge: (1) to increase renewable biomass production without competing with agricultural and natural landscapes; (2) to recycle their waste; (3) to reclaim contaminated or unfertile sites.

The LORVER project, by reconstructing a fertile soil with different nonhazardous wastes with agronomical potential, could help restore brownfields' fertility and hence address those challenges [1].

Its potential environmental and social impacts need however to be quantified.

Objectives and stakes

Life Cycle Assessment (LCA) [2] is a normed methodology inventorying the flows generated by a product over its lifecycle to evaluate its potential impacts (e.g. climate change, ecotoxicity, etc.).

This thesis first consists in (1) the LCA of the LORVER project, (2) the improvement of LCA to better grasp the costs and benefits of LORVER, in terms of landscape preservation [3].

The developed methodology aims to help stakeholders to choose between different solutions to tackle at best their local challenges.

Methodology/ Experimental approach

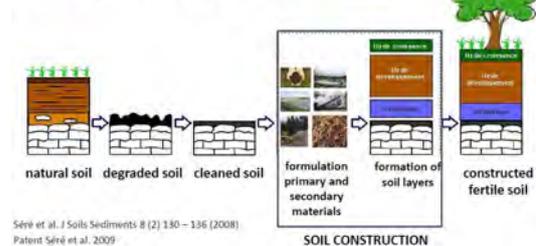
A LCA is conducted on LORVER, from waste transportation and use to build a soil, to the transformation of the produced biomass.

It is compared with two other scenarios where waste are either incinerated or landfilled: one where biomass is produced directly on the polluted site (REF1); one where a soil is constructed with raw materials (REF2).

All three scenarios are calibrated to hit the same amount of biomass produced, in order to make the comparison meaningful.

Illustration: Conceptual scheme of the LORVER project

Combination of materials of urban or industrial origin to create pedologic profiles to restore soil functions



Main results

In the specific context of the research project, transport of waste has a stronger environmental impact in a LORVER scenario than in a REF1 scenario, mainly due to higher distances. Expected tenfold higher yields than in REF1 would however decrease pressure on local landscapes.

Scenario REF2 is yet to be assessed precisely. It could either be intermediate between REF1 and LORVER in terms of emissions of pollutants, or the worst case scenario, if distances traveled by the raw materials exceeded 100 km.

An assessment method had been chosen to evaluate the ecological value of the commodities preserved by LORVER, translated in resources used for their formation [4]. This choice has been discarded, mainly due to the low availability and reliability of the data required.

Future work will aim to (i) refine current inventories with empirical data; (ii) focus on the provision of ecosystem services by preserved commodities, as a more qualitative method than what is currently available in common LCAs.

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2015



Processes of mobilization/immobilization of metals in an agrosystem designed for metal recycling from biomass

Marie Rue (2nd Year of PhD)

M.O. Simonnot, J.L. Morel (LSE)

Processes for Environment, Safety and Resource Recycling



General context, scientific issues

The valorization of wastelands and materials is a major challenge for the regions that have undergone important industrial changes. Nowadays this is evolving towards the development of ecosystem services on these lands and materials. This work consists in the use of plants able to extract metals from the soil. These plants are called hyperaccumulator (HA) plants. Metal extraction can be done *in situ* or on a constructed soil made from waste materials (urban and industrial byproducts). My study focuses on the mobility of nickel (Ni) contained in the materials, evaluating their potential transfer to the plants for **agromining**.

Objectives and stakes

The selection of powerful individuals is one of the agromining improvements. These selected individuals will be able to integrate Ni recovery processes by hydrometallurgical processes, taking into account the constraints related to the purification of the product.

Applications of this work will be considered for multi-contaminated matrices, with special attention for tolerance to high concentrations of metals and co-contamination.

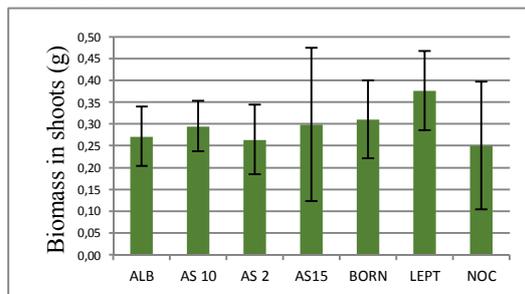
Methodology/ Experimental approach

We cropped HA plants, under controlled conditions, to select the best candidate, *ie* with highest biomass and concentration in Ni in their shoots. We cropped 4 species and several populations. In parallel, we mixed different materials (sludge, amendments, soil...) selected for their high Ni concentration and/or interesting agronomic properties. Then we test the ability to growth of these plants on these mixtures.

After cropping, plants are analysed with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to evaluate their concentration in metals and therefore their capacity to extract metal. Soil is analysed as well to assess metal mobility.

Once we select the optimum formulation and the best performing plants we will test the system at the plot scale.

Illustration



Biomass in shoots of seven populations (N=70).

Leptoplax emarginata (LEPT), *Alyssum murale* (AS2, AS10, AS15, ALB), *Noccaea tymphaea* (NOC), *Bornmuellera tymphaea* (BORN) from the Balkans.

Main results

- The cropping of HA plants shows that the intra- and inter- population variability of Ni concentration are very high. But *L. emarginata*, *B. thymphaea* and some populations of *A. murale* offer a high potential for Ni phytoextraction under our experimental conditions.
- The tested mixtures show that the presence of biochar (obtained from biomass pyrolysis) as an amendment, increases the potential of vegetalisation of the mixture and the transfer of metal to the plants.
- Despite the toxicity of the used materials (metal sludge ...) we can get the development of plants and the extraction of Ni. These results are very promising. Now we should test the cropping of longer time (full cycle of plant development) and test other waste to enable Ni extraction on a wide range of materials.

References

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2015



Thesis subject

Rémi Suaire (3rd year)

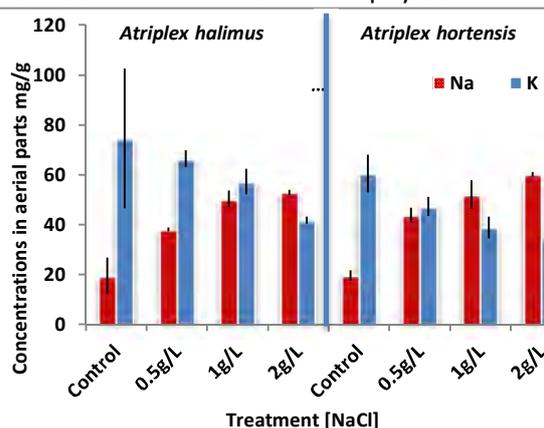
Marie-Odile Simonnot Ivana Duricovick (CEREMA)
Processes for Environment, Safety and Resource recycling



General context, scientific issues

Road deicing salts have been described as a serious environmental hazard due to their high mobility and documented toxicity for numerous species. Their transfer through wet detention ponds is suspected to be the cause of trace metals remobilization and these ponds do not treat deicing salts since they remain most of the time diluted. Several attempts have been made to develop specific treatment systems, but phytodesalination still needs to be investigated

Illustration Accumulation in halophytes



Objectives and stakes

- Establish a mass balance of deicers transfer through treatment systems
- Assess deicers effect on metals remobilization
- Test several halophytes for phytodesalination of road runoff

Main results

- Sodium chloride, used as a deicing salt, has a significant effect on metal mobility in roadside soils. Mechanisms involved remain unclear but ion exchange is considered as a minor component whereas colloids dispersion is a major one. The effect on remobilization within wet detention ponds was not significant.
- Between 30 and 55 % of deicing salts spread on the road were collected in the pond, although this depends on road design and meteorological conditions.
- Geochemical composition of soils nearby and roadsides have a great importance in mitigating deicing salt effects.
- *Atriplex halimus* and *Atriplex hortensis* L. displayed promising results regarding tolerance to road runoff, phytoextraction of sodium and chloride and trace metals phytostabilization.

Methodology/ Experimental approach

Water and sludge samples were collected from a wet detention pond along a French national road. Water quality, deicers and trace metals concentration were measured and confronted with results obtained with sequential extractions and leaching assays on sludge samples. A mass balance of deicers transfer through the pond was calculated using a continuous measure of conductivity of road runoff.

Results on water and sludge quality were used to design an experimental setup to assess halophytes tolerance and remediation abilities regarding road pollutant (NaCl as a deicing salt and trace metals). Complete germination, growth and bioaccumulation assays were developed and potential sodium, chloride and trace metal uptake measured.

References

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2015



Multiscale study of biogas production in a wastewater treatment reactor

BEJI Olfa (First year of PhD: 2014)

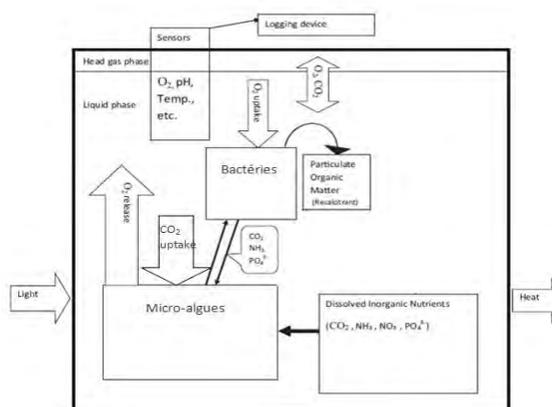
Supervisors name: Souhila PONCIN & Huai Zhi LI



General context, scientific issues

- Coupling of bacteria and microalgae for the wastewater treatment and production of valuable biogas sludge
- Multiscale approach to study multiphase reactors involving three phases: microalgae, water and gas
- Interactions and relationship between multiphase flows and biological performance as well as mass transfer

Illustration (result, methodology or context)



Objectives and stakes

- I- Study of the $\text{CO}_2 \leftrightarrow \text{O}_2$ gas exchange into a closed bacteria / algae micro-ecosystem.
- II- Purification of biogas by using of microalgae => Methane production.

Main results

- Kind of microalgae was selected for our experiments.
- A first setup of column type was built up and operated.
- Micro and mesoscale reactors are being constructed.
- Flow fields around rising bubbles and microalgae are expected by means of PIV technique.
- Rheological characterization of reacting media is envisaged.

Methodology/ Experimental approach

Describe the methodology (theoretical) and the experimental approach you will or have already developed in your work

Multiscale approach is employed in this thesis: macroscale with a 3D multiphase reactor; mesoscale near 2D reactor and finally microscale near 1D reactor. The coupling between the multiphase hydrodynamics and the biological performance will be linked to optimise the process.

The biological aspect is studied by the INSA-Tunis and the multiphase hydrodynamics is considered in the LRGP, mainly by means of a PIV technique, a camera and a rheometer.

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2015



Optimization of the microporous and its impact on aging and water management in fuel cell

MARIEM BELHADJ (2nd year)

François Lopicque, Caroline Bonnet
SysPol



General context, scientific issues

This thesis CEA-Tech is co-supervised by the LRGP and the Cea-Liten with foundry from Region Lorraine. Polymer Fuel Cell Membrane (PEMFC) is considered an alternative energy for stationary and transportation applications 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

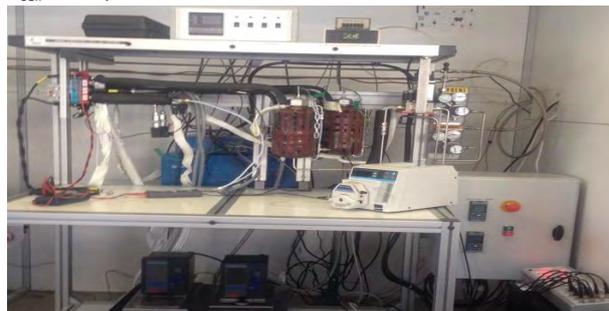
The performance of PEMFC depends on the catalyst activity and the quality of its various components including the gas diffusion layer (GDL). In this study the impact of microporous layer (MPL), one part of the GDL, on ageing and water management in fuel cell is investigated. The MPL hydrophobicity depends on the location 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 European standard conditions (NEDC). 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

test bench for fuel cell cycling (one cycle's duration = 20 min), operating conditions ($\lambda_{H_2}-\lambda_{air} = 1.2-2$, RH= 50%, 1.5 bar, $T_{cell}=80\text{ }^\circ\text{C}$)



Main results

The electrochemical measurements have been conducted in a 100 cm² fuel cell. The AME with GDL and MPL layers were prepared in Cea-Liten. To evaluate GDL/MPL degradation, 1100 cycles have 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 cycling, the fuel cell response decreases in a linear manner. The regularly voltage loss indicates the degradation of the GDL-AME. 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. Fuel cell properties are affected by ageing operation. Impedance spectroscopy is performed to evaluate the double layer capacitance, the Ohmic resistance, charge transfer and mass transfer resistances.

References

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2015



Energy production and storage: From DSSCs to a photo-reloadable battery

Robin Cisneros (3rd year)

Fançois Lapicque, LRGP - SysPol
Marc Beley, SRSMC, PhotoSens



General context, scientific issues

In a general context of decreasing fossil resources, there is an urge of finding new sources of energy and new ways to store it. Sunlight offers great hopes, but the way to produce photovoltaic panels without back pollution and to a lower cost is still a problem. Nevertheless, Grätzel proposed in 1991 a new way to convert photon to electron through a low cost screen-printed device, mimicking photosynthesis: the dye sensitized solar cell (DSSC) [1]. For energy storage, lithium although extensively considered, is a rare element and cannot solve the problem alone. Renewable way had then to be found for this purpose.

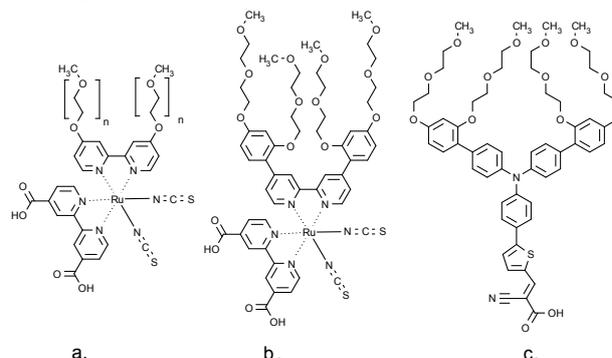
Objectives and stakes

The aim of this work is to find a pathway between the DSSC and a photo-reloadable battery, using common, affordable materials avoid further emission. The first point is to design a photo-electrode for aqueous media, through synthesis of hydrophilic photo-sensitizers, among other things. The second point is to design a battery prototype, and select a set of redox couples to implement into it.

Methodology/ Experimental approach

We have first imagined a spectroscopic technique, based on electrochemical impedance spectroscopy (EIS) coupled to wavelength scan, to identify and quantify the different parasitic electronic processes e.g. electron recombination, involved in DSSC and their dependence to light wavelength and power. Next, we have studied through this technique, the benefit of co-adsorbents to limit the significance of these undesired processes, and select the one which is the most suitable to set a photo-electrode working in aqueous media. Also, we synthesized hydrophilic photo-sensitizer based as on purely organic compounds as on metal transition complexes. Finally, our photo-electrode was implemented in a device of an original design for energy production and storage from sunlight.

Illustration: Hydrophilic sensitizers synthesized during this study.



Main results

We successfully designed and set a new technique to identify and quantify drawback processes in a DSSC through EIS with a wavelength scan, which has been published in *Electrochimica Acta* [2].

An efficient co-adsorbent has been identified to avoid water degradation by photo-activity of the photosensitive electrode and limit recombination. A paper on this process to be submitted to PCCP is in preparation.

We have synthesized new hydrophilic Ru-complexes as photo-sensitizers, which exhibited interesting results when involved in water-based DSSC. This work will be shortly submitted to *Dalton Transactions*.

Finally, we have designed and constructed a 16 cm² photo-reloadable battery from low cost materials. This device is representing such a breakthrough in the production and storage of energy. First tests are promising, and next steps of the research on this device are to raise its power density, increase the number of cycles and lower the loading time. The publication or the protection of this device through a patent is in discussion. Thanks are due to Prof. em. J.F. Fauvarque (CNAM) for his large contribution

References

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- [2] Cisneros et al., *Electrochimica Acta*, 2015, 171, 49-58
- [3] Cisneros et al., *Chem. Eng. Trans.*, 2014, 41, 193-198

<p>2015</p> 	<p>Elaboration de matériaux à très haute porosité par des procédés mettant en œuvre des fluides supercritiques</p> <p>RUIZ GONZALEZ, Francisco (Year of PhD 2012) Huai Zhi LI and Michel PERRUT Laboratoire Réactions et Génie des Procédés CIFRE with SEPREX S.A.S.</p>	
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General context, scientific issues

An « AEROGEL » is a highly porous solid material obtained by drying a « sol-gel » using the so-called « supercritical drying process». This work is mainly focused on silica-based material in order to obtain silica aerogels, possibly reinforced by fibres or mats, for use as super-insulation materials. In particular, this thesis aims to developing a new process economically competitive in regards with the production of other well established insulation materials.

Illustration (result, methodology or context)




Scheme of the experimental setup for aerogel fabrication at Séparex S.A.S. (left) and an aerogel obtained (right).

- Objectives and stakes**
- The work develops satisfactory steps forward:
- Reduction of processing duration.
 - Reduction of the total energy consumption of the process.
 - On-line hydrophobization process.
 - Scale-up to industrial manufacturing of the process.
 - New drying process for granular aerogels.

- Main results**
- Various aerogels (hydrophobic and hydrophilic) were obtained and characterized.
 - Reduction of processing duration by half was realized.
 - Significant reduction of the total energy consumption of the process was achieved.
 - New drying process and scale-up were realized

Methodology/ Experimental approach

Describe the methodology (theoretical) and the experimental approach you will or have already developed in your work

- Design and construction of equipment for high-tech processes with supercritical fluids.
- Characterization and analysis of produced aerogels and process modeling in cooperation with Prof. Li of LRGP and Mines Paris.
- Participation and development in four European projects of the 7th framework programme, AEROCOINS (www.aerocoins.eu), AerSUS (www.spi.pt/aersus/), RESSEEPE (<http://resseepe-project.eu/>) and HIPIN (<http://www.hipin.eu/>). All programs concern the research and development of diverse aerogels-based materials for different applications from insulation of houses to insulation of spacecraft and satellites.

References

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<p>2015</p> 	<p>CO₂ sequestration by mineral carbonation in steel sector Treatment of carbonate slurry for recovery of valuable metals</p> <p><u>Laura TURRI (2nd year)</u> François Lapicque, Hervé Muhr SysPol</p>	
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General context, scientific issues
Valorco is a project coordinated by ArcelorMittal, in order to develop steel industry with low CO₂ emissions. The project consists of a fully integrated carbon dioxide capture and sequestration process by mineral carbonation, an alternative in which CO₂ is chemically stored in solid carbonates, thermodynamically stable. Olivine is used as mineral feedstock, a magnesium-iron silicate (Mg,Fe)₂SiO₄ that also contains small amounts of other metals including Cr, Al and Ni.

Illustration
MEB/EDS analysis: Products obtained after carbonation in standard conditions (reaction time 90 min ; 100 bar ; 175°C ; S/L ratio: 25% ; additive NaHCO₃ 0,64M)

Objectives and stakes
To ensure environmentally responsible process, the slurry obtained after carbonation must be managed as a valuable waste. To make this project profitable, the study is focused on the separation technologies for recovery of pure valuable compounds. To consider the optimal separation, the challenge is based on the combination and the coordination of separation processes. Requirements for the valuable products depend on potential markets. Pre-treatment of the olivine could be an alternative for separation of Ni and Cr before carbonation reaction.

Main results
The valuable products of the slurry are mainly present in solid fraction of fine particles (<100 µm). They are mainly composed of MgCO₃ and Si, whose average size is respectively of around 10 µm and 50 µm. Nickel, iron and chromite are present in trace quantities. Maximum efficiency of separation techniques requires a particle size and optimum operating conditions [1]. For fine particles (<100 µm), physico-chemical separation based on surface phenomena is preferred to recover chromite from olivine [2]. Chromite selective flotation is achieved in a lab-scale column using CTMAB as collector in a pH solution of 11. Preliminary tests conducted with chromite samples revealed that 100 % of the particles are recovered after 1 h of flotation. For ultrafine particles (<10 µm), particles are agglomerate by flocculation to enhance their separation. Electrostatic separation based on the different charges between two solids can be considered for the separation of SiO₂, negatively charged, and MgCO₃, positively charged [3]. Separation of nickel present as carbonates may be considered by leaching in the presence of an ammonia solution. However formation of mixed Mg, Fe, Ni carbonates in the magnesium matrix compromises

Methodology/ Experimental approach
Products characterization is essential to consider the separation, to optimize the carbonation reaction and to improve the product value on the market. The methodology of characterization is based on physical, chemical, quantitative and qualitative analysis: (i) Particle size distribution to develop the appropriate separation process, (ii) Pozzolanic activity related to BET area, (iii) Thermo-gravimetric analysis to determine the carbonation rate of olivine, (iv) MEB / EDS to analyse the visual aspect of particles and the relative distribution of elements, (v) Leaching of solid phase and ICP-MS to quantify the elements.

References
[1] Rama Murthy, Minerals Engineering , 2011, p 375-380.
[2] Feng and Aldrich, Hydrometallurgy, 2004, p 319-325.
[3] Wang et al., Innov. food science & tech., 2014, p 360-365.



2015



Biogas valorization

Wedraogo, Tarsida Nicolas (ATER)

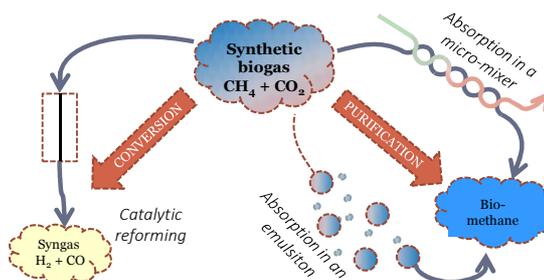
H.Z. Li, S. Poncin
Syspol (Axe 1)



General context, scientific issues

Biogas produced by anaerobic treatment of wastewater is an interesting energy resource from an environmental and economic point of view. The process of methanisation yields a gas composed of 55-70% of methane and 30-45% of carbon dioxide along with impurities such as hydrogen sulfide. It can be burned on site to provide heating or electricity, but there are other value adding uses. For example, biogas can be injected into a grid of natural gas for transport provided that the methane content reaches 95%.

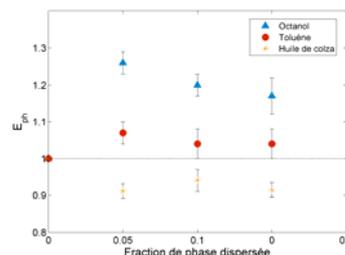
Illustration



Objectives and stakes

Design and investigation of energy efficient, sustainable, innovative processes for biogas valorization

Main results



During the experiment of absorption into emulsions, an intensification of mass transfer with octanol and toluene was observed. These results could be partially explained by surface tension conditions.

In the micro-mixer, experiments were performed to measure the mass transfer coefficient k_{La} . The values obtained can be as high as 3.5 s^{-1} .

The dry reforming of biogas was successfully carried out without any measurable carbon formation.

Methodology/ Experimental approach

Two main processes were investigated: the production of bio-methane and the production of bio-syngas.

Bio-methane

Two innovative absorption processes were studied: (1) absorption into emulsions where dispersed phase droplets can enhance the transfer of carbon dioxide in the liquid; (2) absorption in a micro-mixer where the micrometric dimensions of the reactor provide high mass transfer performances.

Bio-syngas

Biogas can be transformed into syngas by dry reforming. This reaction was carried out in a narrow channel with a $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst.

References

T.N. Wedraogo, S. Poncin, J. Wu, Huai Z. Li. *Intensified biogas purification in a stirred tank*. Chemical Engineering and Processing: Process Intensification 86, Dec. 2014.

2015



STUDY ON MICRO-SCALE INTERFACE PHENOMENA

WU, Yining (Year of PhD 2012)

Huai Zhi LI and Youguang MA (co-tutelle)
Laboratoire Réactions et Génie des Procédés
École Nationale Supérieure des Industries Chimiques



General context, scientific issues

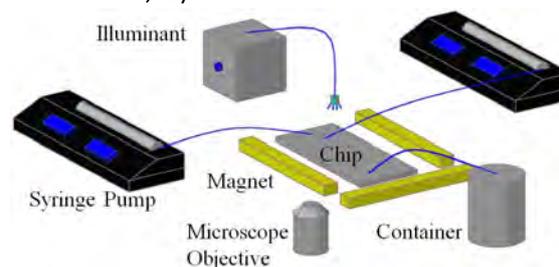
Describe the general context and the main issues of your work

This thesis investigated the active control of the ferrofluid droplets' generation, breakup and coalescence processes under magnetic field.

The generations of satellite droplet during the formation, breakup and transporting of main droplets in microfluidic channels were investigated.

Illustration (result, methodology or context)

A figure that can illustrate your work (set-up, main result, ...)



Scheme of the experimental setup for microsystems.

Objectives and stakes

- To actively control the formation, breakup and coalescence of droplets (bubbles).
- To gain insight into the dynamics of the formation of satellite droplets.

Main results

- The volume and the formation frequency of ferrofluid droplets can be actively controlled by the magnetic field.
- The breakup period and the asymmetry degree of breakup of ferrofluid droplet can be precisely controlled by the magnetic field.
- The size of the satellite droplet is proportional to the capillary number of the continuous phase.

Methodology/ Experimental approach

Describe the methodology (theoretical) and the experimental approach you will or have already developed in your work

Droplets (bubbles) were formed in microchannels or at the end of blunt needle. Liquid was delivered from syringes (5 mL, 10 mL and 60 mL, Hamilton, Germany) by a syringe pump (Harvard Apparatus, PHD 22/2000, USA). Gas was fed by a N₂ cylinder and the flow rate was controlled by a high precision micro-metering valve (KOFLOC, Japan). High-speed cameras were used in our experiments to record the behaviors of droplets (bubbles). Then the images obtained were analyzed with different self-programmed code by Matlab.

References

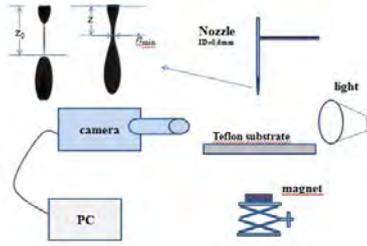
- Y. Wu, T. Fu, Y. Ma, H.Z. Li, Droplet formation and breakup dynamics in microfluidic flow-focusing devices: from dripping to jetting, *Chemical Engineering Science*, 2012, 84, 207-217.
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- Y. Wu, T. Fu, Y. Ma, H.Z. Li, Active control of ferrofluid droplet breakup dynamics in a microfluidic T-junction, *Microfluidics and Nanofluidics*, 2015, 18, 19-27.

<p>2015</p> 	<p><u>Studies on the ferrofluid drop behaviors: formation, coalescence, and manipulation</u></p> <p>JIANG, XIAOFENG (Year of PhD 2014)</p> <p>Huai Zhi LI LRGP-CNRS-ENSIC</p>	
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General context, scientific issues Describe the general context and the main issues of your work

Studying an individual drop is an effective and bottom-up approach to understand complex phenomena involved in numerous domains such as emulsion production, inkjet printing, raindrop, as well as electrosprays. The scarcity of the basic knowledge of the ferrofluid drop breakup, coalescence and manipulation hinders the widely academic and industrial applications.

Illustration (result, methodology or context)



Through experimental analyses, the pinch-off process of ferrofluid drop exhibits self-similar behaviors.

- Objectives and stakes**
- Study the dynamics of the breakup and coalescence process
 - Manipulate the ferrofluid drop to move in presence of barriers and on various surfaces

- Main results** If you don't have results yet, you can describe what are your expected results
- The ferrofluid drop pinch-off shows finite-time singularities and self-similar behaviors. The exponent of power law for the minimum neck diameters versus remaining time exists in the scope of (0.7-0.8).
 - We hope the new results from the coalescence and manipulation processes.

Methodology/ Experimental approach
Describe the methodology (theoretical) and the experimental approach you will or have already developed in your work

The whole work will be experimentally preceded and a high-speed digital camera will be used to observe the morphological evolution of ferrofluid drops during the formation, coalescence and manipulation processes. The drops will be formed in air at the outset of a needle. The drop manipulation will be conducted on specific surfaces and under various operating conditions, in particular different magnetic fields. The images obtained can be analyzed with Matlab.

References

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- E. J. H. Richard F. Day and John R. Lister, Self-Similar Capillary Pinchoff of an Inviscid Fluid, *Phys. Rev. Lett.*, 80 (1998) 704-707.
- N.T. Nguyen, G. Zhu, Y.C. Chua, V.N. Phan, and S.H. Tan, Magnetowetting and Sliding Motion of a Sessile Ferrofluid Droplet in the Presence of a Permanent Magnet, *Langmuir* 2010, 26(15), 12553–12559

Intensification, Optimization And Architecture Of Processes



LABORATOIRE
REACTIONS AND



REACTIONS ET GENIE DES PROCEDES
CHEMICAL ENGINEERING LABORATORY

2015



Modelling of CO₂ capture by amine solvents using hollow fibre membrane contactors

David Albarracin (3th year)

Sabine Rode, Bouchra Belaisaoui
EMSP



General context, scientific issues

Post-combustion CO₂ capture is an important strategy in limiting the greenhouse effect. One of the most studied chemical solvents for CO₂ capture is monoethanolamine (MEA) [1]. The reduction in size of the equipment is indeed of primary importance in order to decrease the capital cost of the installation.

In laboratory conditions for the absorption step, the intensification can be achieved using hollow fibre membrane contactors (HFMC) rather than packed columns [2]. However, the performance of the HFMC in industrial conditions is still unknown. In addition, current models are not adequate to simulate the process for these particular conditions.

On the other hand, intensification studies dedicated to the stripping step have been rarely reported. Furthermore, to our knowledge, the stripping section using HFMC has not been addressed in the literature under industrial conditions.

Objectives and stakes

This work claims to:

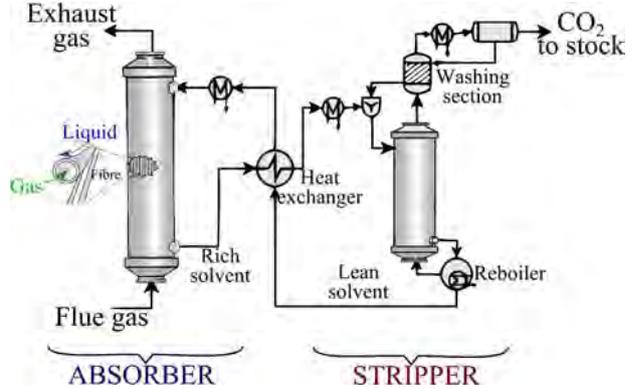
- Identify the optimal modelling approach for the whole process.
- Estimate the intensification potential of HFMC for both, the absorption and the stripping step in industrial conditions.

Methodology/ Experimental approach

The methodology takes into account modelling of varying degrees of complexity (i.e. from one - dimensional (1D) and isothermal to two dimensional (2D) and adiabatic). Then, the influence of the geometric characteristics of HFMC are studied by simulation, for a particular set of operating conditions, which corresponds to industrial conditions used for packed columns.

The simulation results, for the absorption step are compared to those obtained experimentally in-situ.

Illustration:



CO₂ postcombustion absorption-stripping cycle, using HFMC

Main results

When common laboratory conditions (low amine conversion and fresh solvent) are applied, isothermal and adiabatic simulations lead to comparable results in terms of contactor performance.

Adiabatic simulations in industrial conditions highlights the occurrence of significant temperature peaks in the contactor.

Because of the significant temperature peaks and rapid heat transfer in microporous membranes, capillary condensation and thus membrane wetting may occur. These phenomena will deteriorate the contactor performance.

The 1D approach provides almost the same results than those of 2D approach with significant lower calculation times.

The use of fibers with an external radius of less than 400 μm is necessary in order to obtain a significant intensification for the absorption step.

References

- [1] P. Luis et al., *Prog. Energy Combust. Sci.*, vol. 38, pp. 419–448, 2012
- [2] E. Favre et al., *J. Membr. Sci.*, vol. 407–408, pp. 1–7, 2012

2015



Surface modification of polymeric membranes by LBL assembly for organic nanofiltration

BASSIL, Joëlle (post-doc)

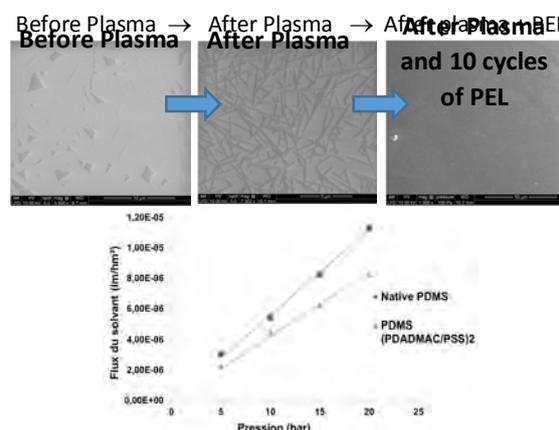
Halima ALEM, Gérard HENRION, Denis ROIZARD
EMSP (Axis 2)



General context, scientific issues

Polyelectrolytes layers based PDMS membranes have attracted strong recent scientific interest in nanofiltration and have reached the stage of being in the forefront among the different types of functionalized membranes, due to the convenient compatibility of the polyelectrolyte-PDMS combination^[1]. This Carnot project consists in developing new composite membranes that could find applications in nanofiltration by using two eco-friendly techniques.

Illustration



Objectives and stakes

- To design and control the formation of thin active layers in order to tailor the membrane properties.
- To evaluate the extent of modifications.
- To determine the separation properties of the modified membranes.

Main results

- SEM pictures and contact angle measurements have shown that 5 min of plasma treatment at 80W as plasma power led to non-defected surface and hydrophilic PDMS.
- The modification with PDADMAC/PSS multilayers gives stable hydrophilic surfaces ($55^\circ \leq CA \leq 80^\circ$). SEM pictures have shown that 5 cycles of PDADMAC/PSS are required for formation of uniform and defect-free multilayers on PDMS.
- The AFM studies and the contact angle measurements indicate that adhesion between PDMS and PEL multilayers is improved by the plasma treatment.
- The preliminary tests of nanofiltration show a decrease in the solvent flow through the membrane after modification of the PDMS with 2 cycles of PDADMAC/PSS.

Methodology/ Experimental approach

1- Plasma treatment

Plasma surface modifications of PDMS were conducted using a microwave post-discharge reactor, using Ar (carrier gas)/O₂ (reactive gas).

2- LBL assembly technique

In terms of subsequent deposition of 2 to 10 cycles of polyelectrolyte, a 3-axis ND-3D robot is used. Polyelectrolyte solutions: PDADMAC (10⁻² mol/L without and with 0.5 mol/L NaCl as supporting electrolyte), PSS (10⁻² mol/L without and with 0.5 mol/L NaCl).

3- Organic nanofiltration

Two experiments are performed with 34.5 cm² and 19 cm². Two solvents will be used: Ethanol and Toluene at 30°C. The membrane is conditioned under 40 bar and then studied at different applied pressure^[2].

[1] Zhu, X.; Guo, S.; Janczewski, D.; Velandia, F. J. P.; Teo S. L.-M.; Vancso G. J. Langmuir **2013**, 30, 288–296.

[2] BenSoltane, H.; Roizard, D.; Favre, E. Journal of Membrane Science **2013**, 435, 110-119.

<p>2015</p> 	<p align="center"><u>Integration of innovative separation technologies in biomass gasification processes</u></p> <p align="center">Etienne Berger (2nd year)</p> <p align="center">Denis Roizard and Guillain Mauviel Membranes, Separations and Processes (Axis#2)</p>	
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General context, scientific issues

Biomass gasification is a promising way to produce energy from renewable sources. The gasification process produces not only gases but also various impurities such as tars. The main uses of the gas (engine, turbine, fuel cell, etc.) require to remove these impurities. The present PhD subject aims at evaluating the ability of new separation techniques to meet this requirement.

Illustration

- Objectives and stakes**
- Measuring the intrinsic performances of the separation techniques
 - Evaluating the ability for these techniques to meet the separation requirements

- Main results**
- Some fundamental properties of tars have been measured. To the best of our knowledge, these properties had never been measured before. So, no comparison with literature is possible. We can anyway observe tendencies that are similar to the ones reported for similar species.
 - We are expecting to measure other properties of tars related to the considered separation techniques.
 - The comparison of the measured properties with the ones of better known species will allow to model the behavior and the performances of the unit operations.
 - These models of separators are expected to bring elements to judge of the ability for the considered techniques to meet the requirements.

Methodology/ Experimental approach

The first step is to measure the physical and chemical properties implied by the considered separation techniques. Due to the unusual nature of the components to be removed, new techniques need to be invented.

Thanks to these properties, it is possible to evaluate the expectable performances of the separation techniques as unit operations.

These unit operations models will be coupled to a model of the whole gasification process in order to evaluate the real interest of the studied separation methods.

References

- Rabou, Luc P. L. M., Robin W. R. Zwart, Berend J. Vreugdenhil, et Lex Bos. « Tar in Biomass Producer Gas, the Energy research Centre of The Netherlands (ECN) Experience: An Enduring Challenge ». *Energy & Fuels* 23, no 12 (17 décembre 2009): 6189-6198

2015



Supercritical fluid extraction of a mixture of *Picea abies* L. and *Abies alba* Mill. : Valorization of high added value molecules of wood biomass

Carole ETCHEVERRY (Engineer CDD)

Danielle BARTH, Laurence MUHR, Denis ROIZARD
Intensification, Optimization & Processes architecture ;
Processes for Environment, Safety and Resources Valorization



General context, scientific issues

The paper industry produces a large amount of biomass residues. It is interesting to recycle these residues due to their concentrations of high-value compounds, such as lignans or other phenolic molecules [1].

Lignans compounds are especially attractive for pharmaceutical and nutraceutical industries.

The project, with an environmental conservation concern, is focused on the extraction with supercritical fluids. Carbon dioxide is the most commonly used solvent.

However, in that event, molecules are polar so they are not very soluble in carbon dioxide. It is then required to use a co-solvent to extract molecules of interest.

Objectives and stakes

In order to establish a method, the aim is to characterize the extracts obtained for comparisons and finally validation of the extraction.

The characterization involves an identification and quantification. As regards compounds of interest, exact quantifications are required for placing the product on the market.

Methodology/ Experimental approach

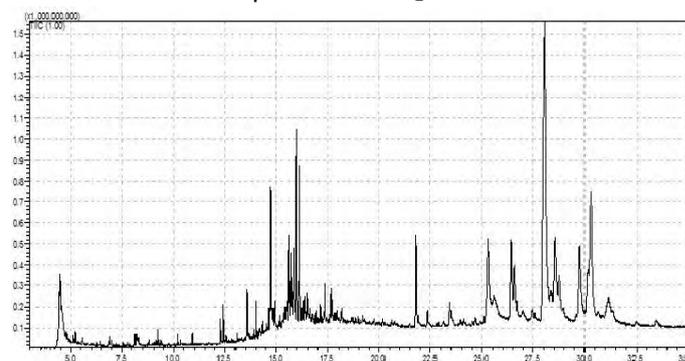
Extracts from mixture of two trees' species (*Piceaabies* and *Abiesalba*) were obtained by supercritical CO₂ extraction.

Analysis are performed by gas chromatography, using a GC system equipped with an apolar column (100% dimethylpolysiloxane) and a mass spectrometer.

The mass spectral library NIST08 is used for identification. To do the accurate quantification, external calibrations are performed with standards.

Illustration:

Example of extract's chromatogram from supercritical CO₂ extraction



Main results

Operating conditions in GC-MS has been established to characterize all extracts [2,3].

Analysis show the presence of many different lignansbut the extraction is not selective to this family. In fact, they are present in proportions : between 33% and 63% in extracts. The rest of compounds are part of terpenes.

However, this method is very interesting because of its high HMR extraction yield (an anti-tumor, anti-inflammatory molecule).

External calibrations of some lignans has been performed.

Futur works will aim to do (i) calibrations of each molecule of interest and (ii) submissive molecules at pharmaceutical norms.

References

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- [2] Yamamoto et al., Journal of Mass Spectrom. Soc. Jpn., 58 (2010), p 195–209
- [3] Journal of Chromatography A, 1112 (2006), p 64-77

<p>2015</p> 	<p align="center">PhD subject</p> <p align="center">Conceptual design for CO₂ capture using membranes</p> <p align="center">Giordano, Lorena (Post-doc) Supervisor: Denis Roizard Membranes, Séparations, Procédés (Equipe EMSP)</p>	
<p>General context, scientific issues</p> <p>Mixed matrix membrane based on MOFs (M4) 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. 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.</p>	<p>Illustration (result, methodology or context)</p>  <p align="center">Post-combustion CO₂ capture</p> <p align="center"><i>CO₂ selective M⁴'s</i></p>	
<p>Objectives and stakes</p> <ul style="list-style-type: none"> • Modelling of transport properties of M4 hollow fiber membranes; • Conceptual design for post-combustion CO₂ capture; • Simulation of one and two-stage membrane processes with multicomponent feed mixtures; • Economic analysis and Life cycle impact assessment 	<p>Main results</p> <ul style="list-style-type: none"> • Modeling of single stage membrane system based on: <ul style="list-style-type: none"> - feed compression; - feed compression and vacuum pumping with or without partial permeate recirculation. • Evaluation of the impact of membrane type and operating temperature on: <ul style="list-style-type: none"> - permeate purity and membrane area; - specific power consumption per unit of CO₂ separated. • Preliminary modeling of dual-stage membrane system based on enricher-concept and retentate recirculation. 	
<p>Methodology/ Experimental approach</p> <p>Membrane gas separation process is simulated using the proprietary software tool M3PRO, properly integrated into Aspen Plus environment, in order to carry out the energy analysis of single and dual stage membrane system configurations. The economic feasibility of membrane separation processes is evaluated by estimating capital (CAPEX) and operating costs (OPEX), as well as their impact on the per unit cost of electricity of decarbonized power plants. The environmental impact of CO₂ capture and compression processes is evaluated with the software Simapro®, using a methodology developed by the Center of Environmental Science (CML).</p>	<p>References</p> <ul style="list-style-type: none"> • Merkel, T. C.; Lin, H.; Wei, X.; Baker, R., <i>Power plant post-combustion carbon dioxide capture: An opportunity for membranes</i>, J Membr Sci, 2010: 359, 126–139. • Favre E. <i>Membrane processes and postcombustion carbon dioxide capture: Challenges and prospects</i>, Chem Eng J 2011;171(3):782-93. • B. Zornoza, C. Tellez, J. Coronas, J. Gascon, and F. Kapteijn. <i>Metal organic framework based mixed matrix membranes: An increasingly important field of research with a large application potential</i>, Micropor. Mesopor. Mater. 166, 67–78, 2013. 	



Optimization of organogel drying process with supercritical carbon dioxide

LAZRAG Mouna (3rd year)

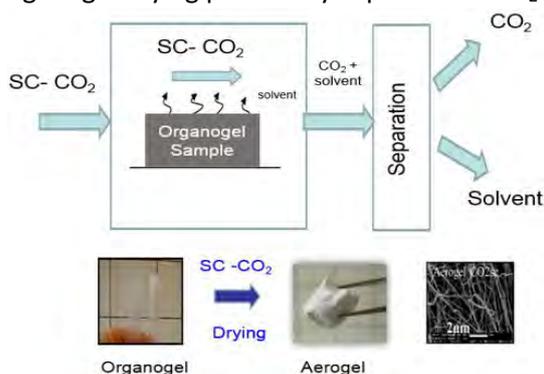
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General context, scientific issues

Drying of organogels, gels composed of an organogelator such as amino-acids dissolved in a solvent, by supercritical carbon dioxide (SC-CO₂)[1] leads to the formation of aerogels, very light solids made of 95% air in volume. These aerogels are expected to be very good heat insulating materials. The challenge now to find the best production process conditions, considering that most of their properties depend on the process carried out to obtain the final product.

Illustration Simplified diagram of the organogel drying process by supercritical CO₂



Objectives and stakes

- Improve the CO₂/ Solvent separation
- Study the drying kinetics
- Ensuring a good process reproducibility
- Automating the process (control of P, T, flow rate)
- Optimize the process

Main results

Cyclonic separation downstream of the organogel drying process studied here is not satisfactory.

The CFD study carried out with ANSYS -Fluent also shows that the liquid is not entrained to the outlet gas, showing that the hydrodynamic is favorable to separation.

The thermodynamic modeling of separation achieved with the Pro II software, using thermodynamic model PPR78 gives recovery rates very close to those obtained experimentally, and hence helps to explain the poor separation in the case of toluene solvent.

Methodology/ Experimental approach

To understand the bad separation of CO₂/solvent when the solvent is toluene two approaches were adopted:

- CFD approach: predict the transport of solvent droplets toward the exit of the cyclone.
- Thermodynamic approach: predict the solvent fraction in the cyclone gas outlet

In addition, to study the drying kinetic a modelling approach with Matlab software, aims to describe the solvent transfer mechanisms in the autoclave and evaluate the optimal drying time [2]

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2015



Selective absorption of tar from producer gas: application to Venturi scrubber for CHP

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General context, scientific issues

Biomass gasification is a promising technology for generation of combined heat and power, chemicals and transportation fuels, e.g. Fischer-Tropsch liquids and synthetic natural gas.

One of the technical key challenge of biomass gasification in fluidized bed is the removal (or destruction) of tars formed inside the gasifier to achieve high gas quality. Indeed, tar condensation and deposition, e.g. sticky solid or oily liquid inside the equipment downstream to the gasifier can cause plugging, fouling and/or

Objectives and stakes

Different physico-chemical methods of tar treatment already exist (absorption, thermal and catalytic cracking, adsorption...). Absorption is considered to be technologically mature. However, the choice of absorption solvent, scrubber optimization and tar loaded solvent management strategy remain a crucial point. The aim of this thesis is to select and study suitable solvent for tar absorption.

Methodology/ Experimental approach

In order to highlight possible solvents for tar absorption, a fast and robust solvent screening methodology based on a multi-criteria analysis was developed [1]. In order to study the performances of the selected solvents, a tar scrubber pilot has been designed and characterized. Venturi scrubber has been chosen as gas-liquid contactor. This type of scrubber develops high interfacial area while being compact and limiting fouling and plugging risks. The selected solvents performances will be measured for raw gas from fluidized bed gasification. These results will be used in order to validate scrubber modelisation. Finally, a technico-economical evaluation of absorption processes will be performed.

Illustration: Pilot plant Venturi scrubber for tar treatment



Main results

Comparison of over a hundred of conventional solvents (alcohols, amines, ketones, halogenated ethers esters, hydrocarbons, chlorinated, and sulfured) allowed to select 2 suitable solvents. To validate this method, experimental study of vapor-liquid equilibria between benzene, naphthalene, anthracene and methyl oleate has been performed and compared with literature and calculated by the model UNIFAC-Dortmund values.

The mass transfer coefficient $k_{L,a}$ of the Venturi scrubber was measured via the sulfites method for realistic operating conditions ($0,1 \text{ s}^{-1} < k_{L,a} < 0,7 \text{ s}^{-1}$). Maximum treatment yields for the selected solvents are between 70% for light tar (e.g. benzene, toluene) and 100% for heavy tar (e.g. pyrene).

Industrial scale-up of Venturi scrubber impact cost of produced electricity. Treatment additional costs calculated via pre-estimate [2] method are between 17 and 150 €/MWh depending on tar treatment yield and solvent management (regeneration, treatment, reuse...)

References

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2015



Membrane surface modification for Organic Solvent Nanofiltration (OSN).

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General context, scientific issues

In the industrial scale, separation processes represents 40-70% of total production cost. In fine chemical industries, they contribute up to 45% of energy cost. Conventional separation processes such as liquid-liquid extraction and distillation are far away from green chemistry. Challenges are to reduce the cost of separation and comply with environment friendly processes. Membrane separation, especially OSN, is a promising technology to replace classical energy intensive separation to an eco-friendly and energy efficient alternative. Therefore we focus on improving membrane performance in the field of fine chemicals separation. Homogeneous catalyst retention by OSN is a good example of such process [1-3].

Objectives

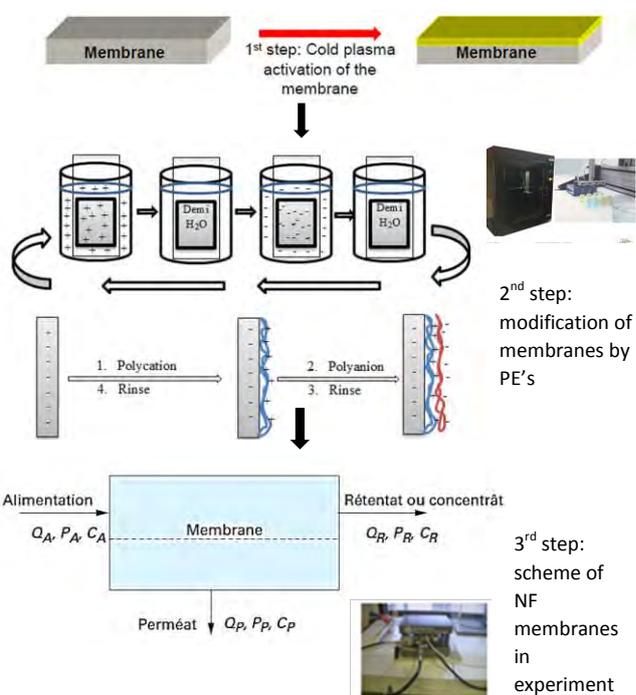
The main objective is to develop new highly resistant and efficient nano-structured membranes for nanofiltration (NF) applications. A protocol for surface modification and characterization will be developed for commercially available NF membranes. Organic solvent fluxes under NF conditions, for example flux of toluene, ethanol etc. will be evaluated. Membrane performances will be optimized in terms of flux and retention behaviour. Finally a correlation between the membrane nano-structure and its performance will be determined.

Methodology/ Experimental approach

The membrane functionalization process is divided in two steps. The first one consists on the use of post discharge plasma to create active molecular species [4]. The second one consists on the layer-by-layer assembly of polyelectrolytes (PE's) in order to obtain a thin nano-structured multilayers film [5]. The membranes will be characterized at each step of the functionalization process by the combination of different techniques as contact angle, microscopic techniques such as SEM, TEM and AFM, XRR. Finally all membranes will be tested for solvent fluxes and retention of model fine ch-

-emicals. Finally, gas permeability reference tests will be conducted to study first the stability of the new composite membranes and secondly the integrity of the membrane. Special attention will be given to control mass transfer of PE's on the membrane and to the transport mechanism through the pristine and modified NF membranes.

Schematic illustration:



Results expected

- (1) Optimum surface activation by plasma will be studied in term of surface energy.
- (2) The influence of the number of bilayers of polyelectrolytes on the final membrane properties will be studied..
- (3) Transport behaviour of organic solvents will be experimentally determined.
- (4) Membrane performance will be evaluated by using model molecules in order to study retention behaviour and to enlighten the retention governing factors.

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2015



**Gas permeation: simulation and experimental study
about CO₂ capture**

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General context, scientific issues

Gas permeation technology is an alternative of growing interest for replacing standard gas separation processes. Membranes become more elaborate so as to improve separation performance and equal or even overtake actual chemical separation processes. CO₂ capture from large sources attars considerable attention as a key strategy to mitigate greenhouse gas emissions. Reducing the energy requirement is the main challenge for CO₂ capture membrane technologies [1].

Objectives and stakes

Experimental study:

Influence of the temperature on different membrane performance

Simulations:

Study cases about the trade-off between permeability and selectivity, the estimation of the energy requirement and the membrane area for different membrane processes...

Study of transport mechanism models.

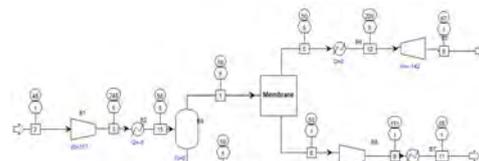
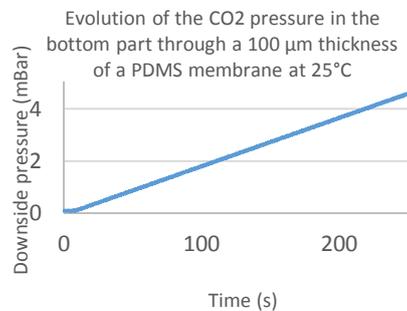
Methodology/ Experimental approach

Time lag experimental study:

Temperature have an impact on the gas sorption and diffusion through a membrane. The performance of three different types of membrane (rubbery and two glassy) at low and high temperature (between -20°C and 60°C) are tested.

Simulations:

On the one hand, new transport mechanism model are developed (sorption diffusion model and reaction diffusion model). On the other hand, Membrane processes are simulated with Aspen Plus software so as to evaluate the energy requirement and the



Membrane simulation model

Main results

Time lag experimental study:

In standard case, the impact of temperature gas sorption and diffusion follows an Arrhenius law. When the temperature increases, gas permeability increases too and selectivity decreases. My expectations are that at low temperature, the selectivity increase could be much significant that the reduction of gas permeability. That results will not follow the Arrhenius law any more.

Simulations:

New transport mechanism models has been developed. My expectations are that results from new simulation models and an experimental data are similar. After we will be able to evaluate the energy requirement and the membrane surface area in order to determine the optimal conditions.

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2015



Gas Membrane Separation Processes for CO₂ Valorization of Blast Furnace Gas (BFG)

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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

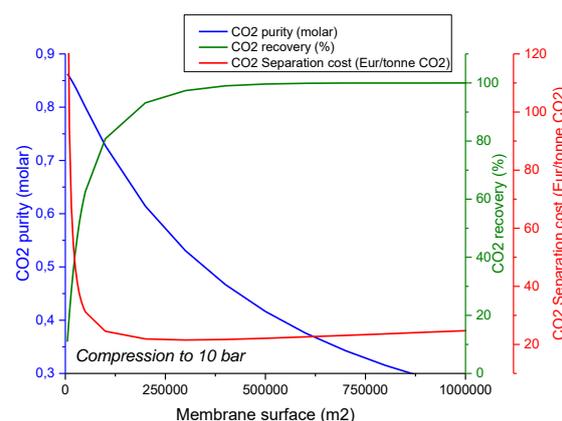
This thesis is carried out within the VALORCO project in partnership with Arcelor Mittal and ADEME. The project aims to reduce total carbon emissions by at least 30%. The objective of this thesis is the conception and design of a gas membrane separation process allowing CO₂ valorization by chemical or 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.

Methodology/ Experimental approach

Data for commercially available membranes are used for the simulation of BFG separation processes by means of a gas permeation simulation tool developed within the laboratory. The effect of operating parameters on the separation performance and cost is studied for different separation architectures in a process simulator software. Experimental runs will be carried out on a laboratory scale membrane module to validate separation predictions and model assumptions.

Illustration

CO₂ purity, recovery and separation cost for permeate enrichment in one stage separation at 10 bar as a function of membrane surface.



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 will be evaluated and operation parameters (membrane surface, compression ratio, number of stages) will be optimized to minimize cost for defined separation targets.

References

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2015



Supercritical fluid extraction of a mixture of *Picea abies* L. and *Abies alba* Mill. : Valorization of high added value molecules of wood biomass

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Intensification, Optimization & Processes architecture ;
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General context, scientific issues

Wood biomass contains high-value compounds that can be extracted previously before combustion for production of energy [1]. These high-value compounds, sometimes called "accidental" or "strange" wood materials, are usually low molecular weight components such as phytosterols [2], oligolignanes [3, 4], lignans [3, 4] and other phenolic compounds [5, 6].

Faced with the need to use environmentally friendly extraction methods, a particular interest has focused on the extraction with supercritical fluids. Carbon dioxide is the most widely used solvent. It is ideal for the extraction of essential oils, lipophilic compounds and slightly polar compounds. On the other side, CO₂ is less suitable in the case of compounds of high molecular weight or very polar molecules because of their low solubility in carbon dioxide. In this case, it is recommended to use modifiers (solvents) which are dissolved in the carbon dioxide, increasing its polarity and allowing the extraction of a greater range of compounds [6].

Objectives and stakes

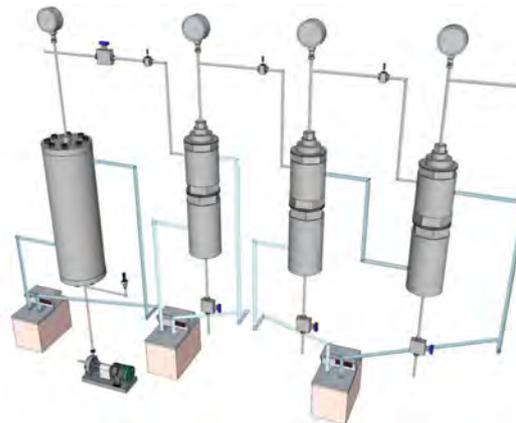
The objective of this work is to validate, optimize, and analyze an environmentally friendly method of extraction of several compounds in the wood. Several operating parameters will be tested in order to study their impact on the profile of biomass extracts.

Methodology/ Experimental approach

A mixture of *Picea abies* L. and *Abies alba* Mill. was provided by Noske Skog Golbey. The sample was divided into two batches (A and B): Lot A consists of the supplied mixture and batch B comprises the fractions after drying at 40 °C.

Several operational parameters of supercritical extraction was studied: water content, temperature, cosolvent (water, ethanol) and pressure.

Illustration: Experimental extraction equipment for supercritical fluid



Main results

In the absence of pre-drying the water content of wood is 42.2%. In the case where the wood was dried, residual water content is 7.7%.

Supercritical extraction conducted without cosolvent presented a very low extract yield. Terpenic compounds are the majority in the extract. In the presence of cosolvent (ethanol), extract yield was higher and enhanced the extraction of lignans. HPLC analysis showed HMR is the major compounds present in ethanol extracts.

Water seems to interfere in extraction and a pre-drying is essential for a higher extraction yield.

Future works will aim to study of (i) separation, (ii) purification and (iii) concentration methods for pharmaceutical application

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2015



Study of PDMS permeability to humidified gases

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General context, scientific issues

The first study of gas permeation through a polymer was conducted by Thomas Graham in 1829.

As well known, the diffusion of small molecules into polymers is dependent on properties of both the polymer and the diffusants.

Gas permeation through a membrane is proportional to the product of solubility coefficient (S) and Fick's diffusion coefficient (D).

In this study, we are interested to PDMS polymer (Polydimethylsiloxane).

The hydrophobicity and rubbery properties of PDMS make it a membrane with good permeability, selectivity and stability [1].

Its main application concerns the use of thin film PDMS to investigate the permeation of humidified gases. [2]

Objectives and stakes

Issue: Confidential

Methodology/ Experimental approach

In this work, we are interested in formulation of dopes ready for film casting, preparation of polymeric membranes and characterization of films properties.

Polymeric solutions (15 wt. %) were prepared by dissolving two monomers, crosslinker, in heptane.

For the preparation, the solution of PDMS was kept in the oven for 4 hours at 60 °C. Then, PDMS solution, containing crosslinker was cast over the support [3].

At last, we are interested on the study of gas transport through polymer membranes by modelling of transport properties.

Illustration:

Preparation of PDMS films by solution casting method [1]



Main results

Issue: Confidential

References

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2015



Study of carbon dioxide capture with a composite membrane contactor: from the absorption to the desorption of CO₂

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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 to develop chemical absorption of CO₂ in absorbing water solutions; within that frame, the use of Hollow Fiber Membrane Contactors (HFMC) present a promising intensification potential compared to conventional gas-liquid packed column. [1]

Objectives and stakes

Composite membrane (i.e. a dense polymeric skin coated on a porous support) will be used for chemical absorption of carbon dioxide because it increases the stability of the capture efficiency over time compare to microporous membrane. Indeed, the dense layer on the liquid side prevents the membrane from wetting [2].

The absorption step with a CO₂/N₂ mixture with vapor content close to the saturated pressure will be investigated to come closer to the industrial conditions. Then, desorption with a composite membrane contactor will also be studied for the first time.

Methodology/ Experimental approach

A pilot is developed to determine water vapor mass transfer coefficient for different membranes (microporous, dense and composite) and several temperatures. These values are obtained by measuring water vapor flux through the membrane module with a capacitive hygrometer. A second pilot is used to study chemical absorption of CO₂: Gaz mixture of CO₂ and N₂, humidified or not, can be prepared in order to study the effect of humidification on capture efficiency.

A third pilot will be developed to study desorption of CO₂ from the absorbent solution in a composite membrane contactor and the results will be compared to conventional stripper.

Illustration:

Membrane contactor pilot used in the laboratory



Main results/expectations

Water vapor mass transfer coefficient (km_{H_2O}) has been determined for microporous membrane, composite membrane and dense membrane. The values obtained are in the same order of magnitude as the ones of the literature, validating the method used to calculate km_{H_2O} . During the absorption, it is possible that water vapor has an effect on selectivity or condenses in the pore of the microporous layer inducing membrane wetting. If these hypotheses are confirmed, the absorption efficiency should be lower with a wet inlet gas than with a dry one. Moreover, if the membrane gets wet it should decrease the stability of the capture efficiency over time by increasing the mass transfer resistance.

References

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2015



Dynamic real time optimization of process

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General context, scientific issues

Optimization is important in science and engineering as a way of finding the best operating conditions. Optimization is typically performed on the basis of a mathematical model (a set of Differential-Algebraic Equations) that could be inaccurate especially in presence of disturbances.

In a context of global competition and saturated markets, it is essential to the process industry to strive for more efficient manufacturing.

Dynamic optimization can be used to determine optimal input profiles for dynamic processes. The optimal inputs determined through model-based optimization will not be optimal for the plant. [1]

Objectives and stakes

Measurements can be used in an optimization framework to compensate the effects of uncertainty [2]. The objective of the thesis is to define an appropriate methodology of dynamic real time optimization for a polymerization batch reactor and validate it. A major characteristic of polymerization reactors is their complex non-linear behaviour. Global optimization will be carried out finally to ensure an overall optimal functioning.

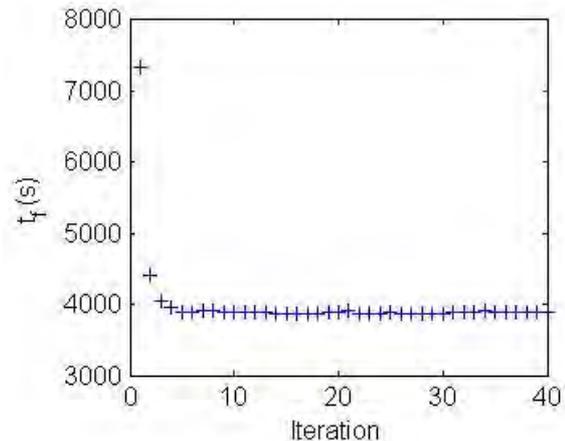
Methodology/ Experimental approach

One of the most used technique for real time optimization is referred as the two step approach. The main idea is to carry a step of parametric estimation followed by a re-optimization using an updated model.

Hence, the measurements can be used to estimate the gradient of the plant to enforce the necessary condition of optimality with a scheme to update the inputs.

Polymerization reactors play a key role in polymer engineering, and the importance of their effective control is well recognized in the polymerization literature [3]. In this study, we focus on the polymerization of a mixture of styrene and waste tire powder developed by another PhD student (Ning Yu GP2).

Illustration: Two step, evolution of the cost function



Main results

We classified real-time optimization schemes and analysed their ability to enforce feasible and optimal process operation by using on-line measurements.

These considerations have been illustrated through the run-to-run optimization of a semi-batch reactor in the presence of model mismatch. One way to perform this is to simulate the reality and to add disturbances in form of parametric uncertainty, structural model mismatch, noises...

An exponential filter of first order have been added to avoid large variations from an iteration to another.

Moreover, we are searching new scheme to perform dynamic real time optimization adapted to batch reactor. The non-linear behaviour of the system and the presence of constraints (due to safety and practical considerations) maintain real conditions to study the performance of those approach.

The results demonstrate that the integration of optimization and control in a real-time framework is a very promising approach for achieving optimal operation (increased productivity, good disturbance rejection...).

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2015



Compact heat exchanger reactor modelling

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General context, scientific issues

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].

Process intensification by miniaturising the heat exchanger reactors allows reducing the limiting phenomena (internal and external mass transfer, heat transfer ...) inherent to catalytic reactions, and as a consequence allows increasing the efficiency [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.

Objectives and stakes

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. The tool will allow the sizing and rating of plate and channel type heat exchanger reactors, and will be validated with experimental and CFD simulation results. This simulation will also allow understanding the physical phenomena occurring in the heat exchanger reactor.

Methodology/ Experimental approach

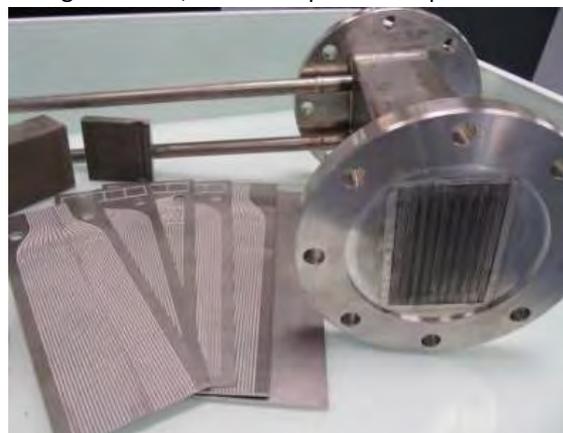
The sizing tool will integrate amongst others kinetics for catalytic reactions, mass transfer correlations and will be interfaced into a commercial heat exchanger simulation software. Novel channel geometries will also be implemented to optimise heat transfer from the hot stream to the endothermic reaction or from the exothermic reaction to the cold stream.

A CFD simulation of both a few channels and the complete unit will be done to study the physical

phenomena at local and global scales respectively (i.e. the external and internal mass transfer, heat transfer, conduction, heterogeneous distribution in the channels ...)

Throughout the project, the tool is expected to be modified to fit at best experimental results under several sets of operating conditions. It is also expected that a newly made heat exchanger reactor will present imperfections of machining, such as plugged or clogged channels, which would lead to a modified reactive and heat transfer area. The program should take into account these imperfections to be as close as possible of the reality.

Illustration: Milli-structured, plate and channel - heat exchanger reactor, with examples of the plates.



Main results

A model of heat exchanger reactor has to be defined to be further implemented into a commercial heat exchanger simulation software. Its validation will be done by comparing its simulated results to those of both experimental and CFD simulation results. The tool may be modified according to this comparison.

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2015



Dissolution of uranium dioxide in nitric medium, towards a model of macroscopic reactors

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Process intensification and improvement



General context

Dissolution, followed by the hydrometallurgical extraction of UO_2 , is a major step for spent nuclear fuel processing. However, there are actually no accurate models for continuous dissolvers.

The present study approach is based on a better understanding of local physicochemical phenomena. The aim is to propose new reactors or to upgrade actual processes for dissolution.

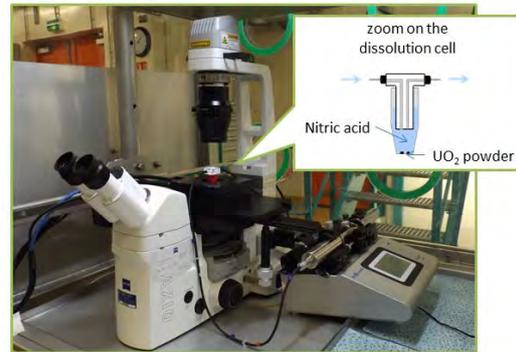
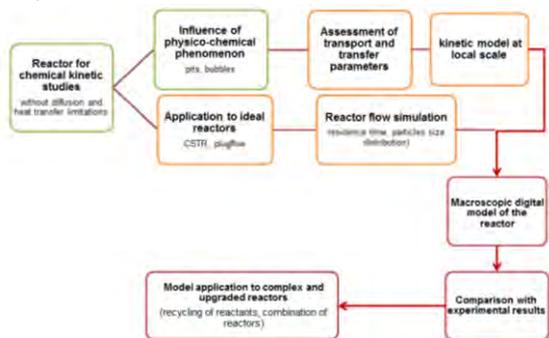


Figure 1: Dissolution cell and microscope for the chemical kinetic studies

Objectives and stakes



Methodology/ Experimental approach

The first goal of our approach is to create a dissolution cell where limitations by diffusion or heat transfer are nonexistent (fig 1).

Chemical kinetic is then studied by following of UO_2 particles apparent area, dissolving in nitric acid, thanks to transmission microscopy.

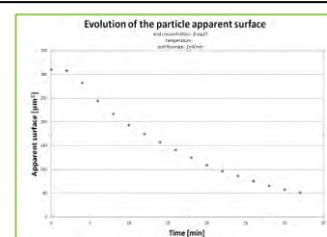
A local scale model of the dissolution of UO_2 pellets already exists [1]. The contributions of heat transfer, grain size and diffusion have to be included.

COMSOL Multiphysic modeling software will be used for reactor flow simulation.

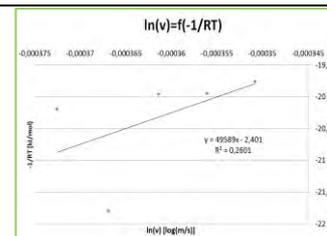
Finally, simulation of the ideal reactor is to be done on Scilab with population balances. An experimental model must be defined to verify the results of the simulation.

Main results

General profile of the area evolution of UO_2 particles. The results show there are several dissolution rates



Dissolution rates are measured for a range of temperatures between 50 and 70°C



- Discuss

Studies of the dissolution with different flowrates and a simulation on COMSOL are ongoing to be sure there is no limitation due to mass transfer.

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2015



Process intensification of halogenated product synthesis and application to industrial continuous production

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Eric Schaer, Jean-Marc Commenge - PRISM



General context, scientific issues

Process intensification has been subject to many works in the past few years, especially in the field of organic chemistry [1].

More particularly microreactors have become a mean of enhancing chemical reaction processes by suggesting the appropriate equipment to fine chemistry reaction while it used to be the reverse way around for decades [2].

Halogenated product synthesis is a good candidate for process intensification as it involves hazardous products with highly exothermic reactions and high yield and specificity are to be met. The present work deals with intensification of the synthesis route of a halogenated product using micro- reactors.

Objectives and stakes

Each synthesis step is analysed regarding heat or mass transfer limitations, reactions kinetics and reaction heat.

After batch experiments are carried out, operating conditions can be suggested to switch to a continuous process, such as a microreactor. Tests are carried out at lab-scale to validate the best experimental conditions before working at pilot scale.

Methodology/ Experimental approach

The synthesis route was first adapted (change of solvent, change in synthesis steps...) to increase its intensification potential. The first reaction steps studied are those having a high intensification potential: experiments in batch with HPLC analyses and temperature recording are carried out to estimate reaction kinetics and reaction heat, before a model can be proposed. This model can suggest the behavior of the reaction system in a continuous reactor, and relevant operating conditions can be identified before tests at lab-scale and seamless extrapolation [3] to pilot-scale are conducted.

Illustration: G1 microreactor designed by Corning



Main results

The two chlorination reactions in the synthesis route are fast and highly exothermic.

They were good candidates for the first intensification studies. Kinetic and thermal data were collected in batch and tests in the G1 reactor were launched, showing good conversion results at temperature near room temperature with short residence times.

Tubing was added at the end of the G1 plates for additional residence time as the 2nd chlorination reaction showed slower kinetics due to steric hindrance. The heat generated by the reaction could be removed with a few plates of G1 microreactor.

These results were successfully transposed to pilot scale using a G4 microreactor, by adapting the design of the system to the desired productivity, keeping constant temperature, ratio of reactants and residence time.

Further intensification study is planned on the hydrogenation step of the synthesis route, involving liquid, solid (catalyst) and gas (hydrogen) phases.

References

- [1] D. Roberge et al. Chem. Eng. Tech. 2005, 28, No. 3
- [2] J.M. Commenge et al. C. R. Physique 5 (2004) 597–608
- [3] A. Vizza, Atochemis Rome Workshop, 2013, 25-27 March

2015



Characterization of micromixing efficiency by the iodide/iodate test reaction in viscous medium

Jordanna Pinot (4th year)

Laurent Falk
PRISM



General context, scientific issues

In chemical reaction engineering, one of the key steps concerns the reactants mixing which must be realized before the reaction step to avoid low conversion and selectivity. Mixing is also important, but very difficult task in viscous medium, for the control of molecular mass distribution in polymerization reactions. Despite many works in this field, no reliable characterization method currently exists for highly viscous media which enables to properly understand the impact of the high viscosity on the reactants mixing.

Illustration : Experimental set-up



- 1 Impeller
- 2 Transmission dip probe
- 3 Injection tube

Objectives and stakes

- New method for quantification of the micromixing efficiency in a viscous medium in stirred tank reactors.

Main results

A new protocol is proposed to study micromixing efficiency in viscous HEC-water solutions. More precisely, the *Villermaux-Dushman* method has been adapted to the study of micromixing in HEC-water solutions by changing the neutralization reaction. The new phosphate buffer has been demonstrated to provide stable operating conditions without impacting the absorption properties of the mixture for in-line monitoring by spectrophotometry. The obtained results present the segregation index as a function of stirring speed for different percentage of HEC until 0.5 wt% corresponding to about 50 mPa.s. HEC-water solutions constitute an interesting system which may be thereafter used to characterize non-Newtonian media by increasing the mass fraction of HEC in water over 0.5 wt %. However, the difficulty is then to take into account this non-Newtonian behavior of HEC-water solutions in the results analysis.

Methodology/ Experimental approach

The used method is inspired by a chemical system based on two competitive reactions, the iodide-iodate reaction system (*Villermaux-Dushman* method), whose products selectivity is a measure of the mixing efficiency.

The approach proposes a new protocol based on a phosphate buffer and the use of HydroxyEthylCellulose (HEC, 720 000 g/mol) as an inert viscosifying agent, exhibiting various interesting properties (no disturbance of the spectrophotometric measure, low cost, low required amount, eco-friendly product).

This agent is almost Newtonian up to 0.25 wt % in water and becomes non-Newtonian above 0.5 wt %. By means of its use, the viscosity of the reactive medium can be raised by around two orders of magnitude while adding less than 1 wt % HEC to the water solution.

References

- Guichardon, P., Falk, L., 2000, *Chem. Eng. Sci.* 55, 4233-4243.
- Pinot, J., Commenge, J.-M., Portha, J.-F, Falk, L., 2014, *Chem. Eng. Sci.* 118, 94-101.

2015



Etude de l'évolution de la réactivité des matériaux porteurs d'oxygène dans un procédé de combustion en boucle chimique

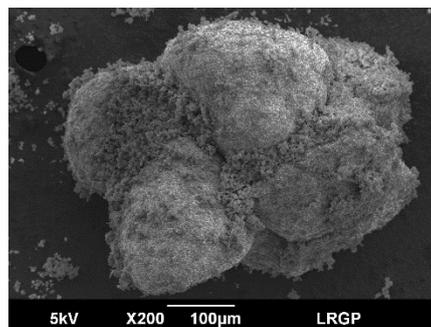
TILLAND Airy (3rd Year)
Ludivine Franck-Lacaze, Eric Schaer
GREENER / PRISM (axis 4)



General context, scientific issues

In order to fight global warming and emission of greenhouse gases, it is essential to improve carbon dioxide capture processes. Among these processes, the chemical looping combustion process allows to generate energy while producing gases with very high concentration of CO₂ which don't need to be treated at a later stage. An improvement of the understanding of the phenomena occurring in this process is necessary to be able to increase its performances.

Illustration

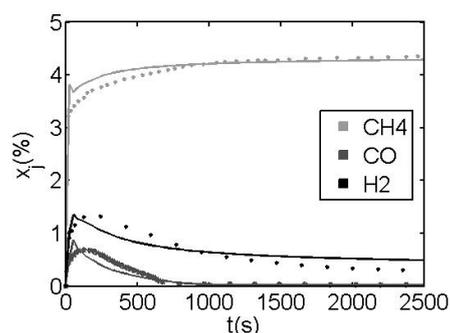


Example of ageing of the material : formation of aggregates and production of fine particles.

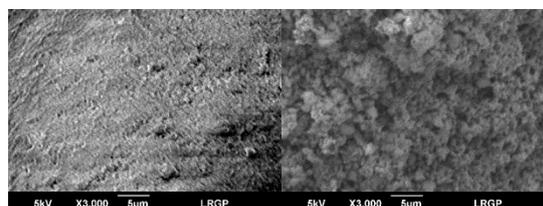
Objectives and stakes

- Determination of the reaction kinetics observed in both steps of the process,
- Modelling of the process,
- Study of the ageing of the material used against time.

Main results



Comparison between experimental (points) and simulated (line) results for an experiment.



Initial after 1.5 hours

Variation of the surface of the material against time (Quantification not done yet).

Methodology/Experimental approach

First the kinetic parameters of the reactions occurring in this process have been determined by comparing experimental and simulated results of combustion of methane with nickel oxide in a perfectly stirred tank reactor.

Secondly, experiments in a fixed bed reactor have been realized to validate the determined kinetic parameters.

Finally, an experimental study of the ageing of the material has been done in the fixed bed reactor. Analysis were performed on the material to quantify the variation of its physical properties. The model of the fixed bed has been modified to take into account of the ageing of the material.

References

A. Tilland, L. Franck-Lacaze, E. Schaer, *Kinetic determination of Chemical Looping Combustion reactions in a continuous stirred tank reactor. Part 1: Reduction of the oxygen carrier*, Chemical Engineering Science, submitted in april 2015

2015



Process design of thermochemical valorization of gases from integrated steelworks

URIBE-SOTO, Wilmar (2nd year PhD Student)

Ph.D. Advisors

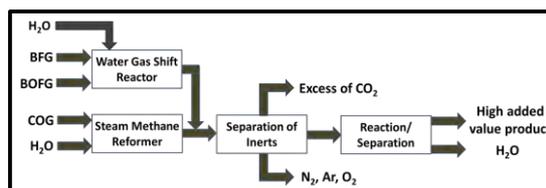
Jean-François PORTHA -Jean-Marc COMMENGE - Laurent FALK
Intensification and Architecture of Processes



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 thermochemical transformation into products with high added value. This particular study focuses on the conception of a valorization pathway of gases from integrated steelworks.

Illustration



General Structure of the valorization scenario.

COG: Coke Oven Gas,
BFG: Blast Furnace Gas,
BOFG: Basic Oxygen Furnace Gas,

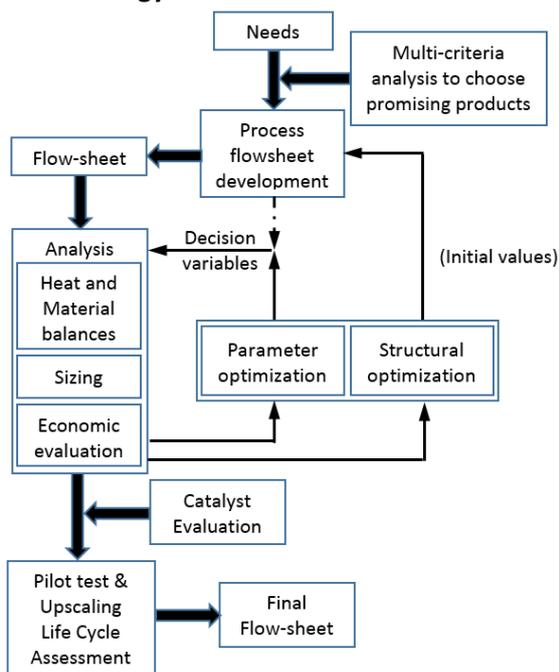
Objectives and stakes

- The identification, evaluation and comparison of the valorization pathways,
- The design and optimization of the selected process,
- The evaluation of industrial catalysts and testing a reactor at pilot scale.

Main results

Several products can be synthesized from the available gases: 10 products have been retained as the most promising paths for further study. A variety of information for each product has been collected. The studied scenario includes the possibilities of hydrogen generation, using Steam Methane Reforming (SMR) or Water-Gas Shift Reaction (WGSR). A multi-criteria analysis was carried out to enable a classification of all products. A review of several alternatives proposed during last years to valorize the available gases was accomplished, thus allowing the development of process flow-sheets that condense different process layouts for the thermochemical valorization of available gases. Future works will aim to optimize the process flow-sheet and to define the most promising process in terms of economic and environmental impact.

Methodology



References

- URIBE-SOTO, W., PORTHA, J.-F., COMMENGE, J.-M., FALK, L., Chemical valorization of CO₂ from steel plants and coke ovens. Large Volume CO₂ Utilization Forum. Lyon, 2014.

Bioprocesses & Biomolecules



LABORATOIRE
REACTIONS AND



REACTIONS ET GENIE DES PROCEDES
CHEMICAL ENGINEERING LABORATORY

2015



Identification of factors implied in the phenomenon of beer gushing and development of a premature detection tool of the gushing risk

Julien Billard (2nd year)
Ivan Marc, Romain Kapel



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

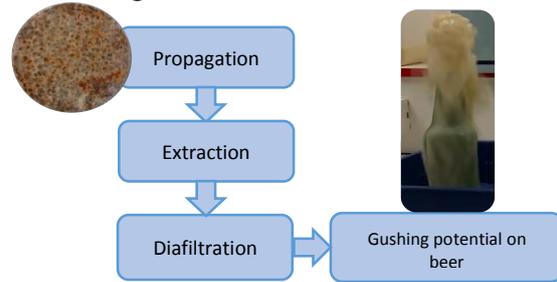
The thesis objectives are to identify the compounds involved and/or at the origin of the beer gushing. Once identified, the point is to:

- determine their origin,
- develop a premature method of detection,
- follow their evolution during brewing process.

Methodology/ Experimental approach

These compounds are currently searched in malt extract naturally contaminated and barley artificially contaminated by fungus [2] involved in gushing. Two methodologies of active gushing compounds research: (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.

Illustration: Extraction procedure to detect a gushing effect of a barley grain contaminated with a fungus named *Microdochium nivale*.



Main results

At first, no significant differences could be seen between malt extract gushing or not by HPLC-RP and SDS-PAGE. On barley extract, only HPLC-RP shows very hydrophobic compounds specific to a fungus strain.

Malt and barley extract has been fractionated by diafiltration, a soft separation technic, to cleanse compounds without distorting or diluting them. After separation by a 5 kDa membrane, the gushing power was preserved and the complexity of sample was decreased by 90 % for a malt extract and 99.5 % for the barley extract. A use of 30 kDa membrane on malt extract showed that compounds between 5 and 30 kDa are involved in gushing. The extraction made on the barley contaminated by *Microdochium nivale* allows to isolate compounds having a strong gushing power (loss of 190 mL on a 330 mL bottle).

The next step will aim to concentrate and to fractionate contaminated barley extracts to isolate and to identify these compounds.

References

- [1] Sarlin et al., J. Inst. Brew., 2005, p 105-111
- [2] Askolin et al., Appl. Microbiol. Biotechnol., 2001, p. 124-130

2015



Performance prediction of ultrafiltration process applied to the fractionation of complex peptide hydrolysates

Alice Bodin (2nd year)

Ivan Marc, Romain Kapel
BioProMo

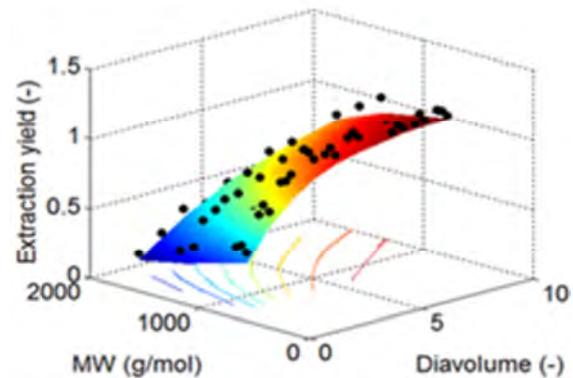


General context, scientific issues

Hydrolysates are complex peptide mixtures obtained by enzymatic proteolysis of proteins from plants or animal resources. They are of great interest for their nutritional and functional (e.g. emulsifying) properties [1]. Hydrolysates may also contain bioactive peptides and are consequently attractive for the nutraceutical market [2].

Ultrafiltration is widely used to obtain peptides fractions with enhanced properties or/and to enrich fractions with bioactive peptides. However, a lack of prediction tools due to the complexity and variety of hydrolysates leads to

Illustration: Experimental extraction yield in targeted peptides (black points) in permeate of diafiltration and surface response of the prediction methodology



Objectives and stakes

A methodology of prediction of extraction yield and enrichment in targeted peptides has been developed by the team BioProMo and validated with one bioactive peptide in an alfalfa white protein hydrolysates [3]. The objective of the thesis is to extend the validation of the methodology using different membranes, hydrolysates, several targeted peptides and various operating conditions.

Main results

The methodology was validated on a 3 kDa membrane with Lactium® (an industrial casein hydrolysate). Several peptides having different molar weight were targeted. Extraction yields and enrichments in permeate and retentate were predicted with relative errors between 2 and 30 % for two operating modes (batch concentration and continuous diafiltration).

Moreover, the impact of operating conditions on membrane calibration was studied. Variations of initial concentration and recirculating flowrate do not impact membrane calibration. Changes of pH and transmembrane pressure induce a slight modification of the membrane calibration, but without significant impact on the global methodology of UF performance prediction.

Future works will aim to (i) study the impact of different hydrolysates on the calibration of membrane, (ii) evaluate the real impact of bioactive peptides enrichment on the hydrolysate bioactivity and (iii) optimize UF process in terms of time of operation and water consumption.

Methodology/ Experimental approach

The methodology of prediction is only based on a size-exclusion chromatography analysis of the initial hydrolysate, its aminogram and a calibration of the UF membrane. Knowing the molar weight of a targeted peptide, extraction yields and enrichments in both UF compartments during batch concentration or continuous diafiltration can be predicted.

To validate the methodology and particularly the membrane calibration, ultrafiltration experiments are carried out with different hydrolysates. Reversed-phase HPLC coupled with mass spectroscopy is used to monitor experimental extraction yields and enrichments in targeted peptides.

References

- [1] Sinha et al., Food chem., 2007, p 1484-1491
- [2] Hernández et al., Int. Dairy J., 2014, p 82-100
- [3] Kapel et al., J. Membrane Sc., 2011, p26-34

2015



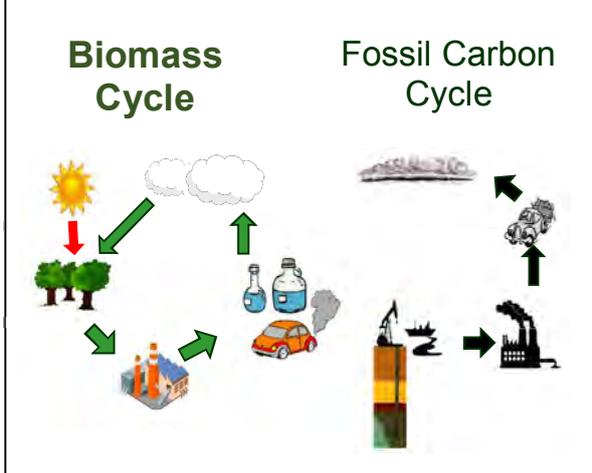
Biofuels and building blocks production by anaerobic fermentation of thermally pretreated cellulose

BUENDIA, Felipe (First Year)

Emmanuel Guedon¹, Anthony Dufour²
¹Bioprocesses-Biomolecules, ²Greener



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. Ligno-cellulosic 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 processes.



Objectives and stakes

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

Expected results

- Improved method for degradation of cellulose by fast pyrolysis to obtain soluble oligosaccharides.
- Fermentation process with *Clostridium acetobutylicum* ATCC 824 at different pH to establish kinetics of growth, substrates consumption and metabolites production.
- For the time being, the base microbial growth kinetics, using glucose and cellobiose, are carried out. These experiences will allow us to identify preferential operation conditions in the fermentation process.

Methodology/ Experimental approach

This work has two stages:

- In order to obtain soluble oligosaccharides from cellulose various techniques of pyrolysis will be implemented [2].
- Biological transformation will be performed by fermentation [1] of carbon substrates obtained in the previous step.

Depending on the substrate utilization, pyrolysis conditions will be adapted to ensure more suitable substrates.

References

- [1] Guedon, Emmanuel. "Analyse du Métabolisme de *Clostridium cellulolyticum*. Importance des Débordements Cataboliques dans la Distribution du Flux du Carbone et des Électrons." UHP - Université Henri Poincaré, 2000.
- [2] Lédé, Jacques, Fabrice Blanchard, and Olivier Boutin. 2002. "Radiant Flash Pyrolysis of Cellulose Pellets: Products and Mechanisms Involved in Transient and Steady State Conditions." *Fuel* 81 (10): 1269–79.



2015



Multifunctional nanoparticles excitable by X Rays for applications in photodynamic therapy

Rima CHOUIKRAT (4nd year)

Céline Frochot (LRGP), Marc Verelst (CEMES)

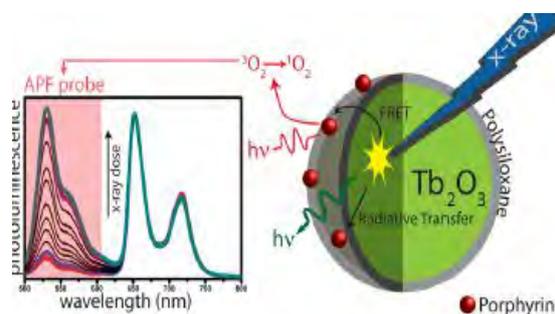
BioProMo



General context, scientific issues

Treatment of glioblastoma multiforme (GBM), a malignant tumor of the brain, is one of the most challenging problems. Photodynamic therapy (PDT) offers a localized treatment approach in which improvements in the local control of GMB may result in significant improved survival. A novel approach is the combination of radiotherapy and PDT, employing scintillating nanoparticles. We suggest the development of nanoparticles excited by radiotherapy for the treatment of malignant cerebral gliomas [1].

Illustration:



Objectives and stakes

The aim of our work is to elaborate new multifunctional nanoparticles (NP) excited by X-ray [2]. We elaborate two kinds of NP: small NP of about 7 nm of diameter with Tb_2O_3 core large NP of about 80 nm of diameter with $Gd_2O_2S:Eu(5\%)$ core. The core is surrounded by an amino-polysiloxane layer in which are covalently coupled the photosensitizers.

The idea is to excite by X-ray the core of the NP to induce PDT effect by the photosensitizer after energy transfer.

Main results

We have presented a biocompatible nanohybrid system including a nanoscintillator and a PS.

For the small nanoparticles, the energy transfer between the nanoscintillator and the porphyrin was demonstrated under UV excitation, and generation of singlet oxygen observed. Combining the effects of PDT and probably radiosensitization, this system can be considered as a good candidate for a significant improvement of radiotherapy efficiency [5].

For the larger nanoparticles, we couldn't demonstrate a possible energy transfer between large nanoparticles and PS. Different problems have been encountered in the study of those nanoparticles, including their large size, their aggregation and their light scattering. Work is planned in the future to reduce the size and the aggregation of those nanoparticles and to improve their physicochemical stability.

The *in vitro* phototoxicity studies using visible light and X ray are in progress. For tumor cells radiosensitized using big nanoparticles, the latter studies could help us prove the presence of a potential energy transfer thus a possible photodynamic activity.

Methodology/ Experimental approach

Photosensitizers synthesis (LRGP)

- Porphyrin: Lindsey method
- Zn-chlorin: porphyrin reoxidation and zinc addition.
A new microwave assisted method has been developed [3]
- Phtalocyanin: cyclotetramerization reaction of phtalonitriles in the presence of a reducing agents [4].

Nanoparticles synthesis (LCPML and CEMES)

- Tb_2O_3 : from chlorid precursors by NaOH addition in polyol medium.
- $Gd_2O_2S:Eu(5\%)$: from nitrate precursors, using procedure based on urea decomposition.

Nanoparticles coating

Stober sol-gel process using APTES, DAEPTS, TEOS

Functionalization of nanoparticles

Covalent coupling using reagents (NHS, EDC, HBTU)

Characterization techniques

HPLC / MS / LC-MS/RMN / DRX / SEM / TEM / 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)

Dark, cytotoxicity, selectivity phototoxicity, PDT effects.

References

- [1] Chouikrat et al., Current Medicinal Chemistry., 2012
- [2] Bulin et al., Journal of Physical Chemistry C. , 2013
- [3] Chouikrat et al., Journal of Porphyrins and phtalocyanins., 2014
- [4] Moussaron et al., Tetrahedron., 2013
- [5] Retif et al.,Theranostics. , (in press)

2015



Targeted PhotoDynamic Therapy

Ludovic COLOMBEAU (Postdoc)

Céline Frochot – Régis Vanderesse
BioProMo - LCPM

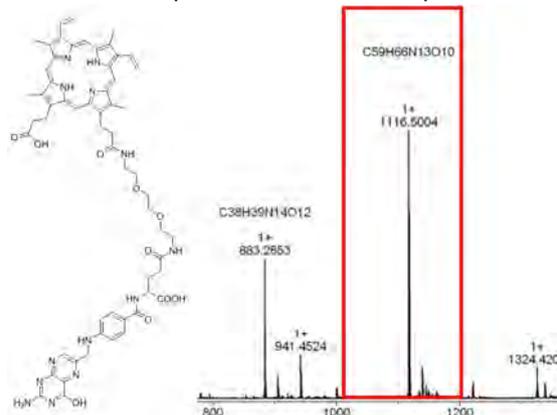


General context, scientific issues

- 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 multiforme (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: PpIX-PEG-FA and MS spectra.



Objectives and stakes

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

Main results

- Project 1: Photosensitizers (with different chemical structure) have been coupled to folic acid, purified, characterized and their photophysical properties studied. The evaluation of the conjugates' stability and biological studies are in progress.
- Project 2: Peptides and peptide-photosensitizer are synthesized and characterized. The evaluation of biological activity (LRP-1 affinity, competition) is in progress.
- Project 3: peptide targeting NRP-1 has been synthesized and coupled to a PS. Its affinity for NRP-1 has been evaluating. Surprisingly, the PS-peptide has a better affinity for NRP-1 than peptide alone. The coupling of this compound onto nanoparticles will be performed in the near future.

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 in 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

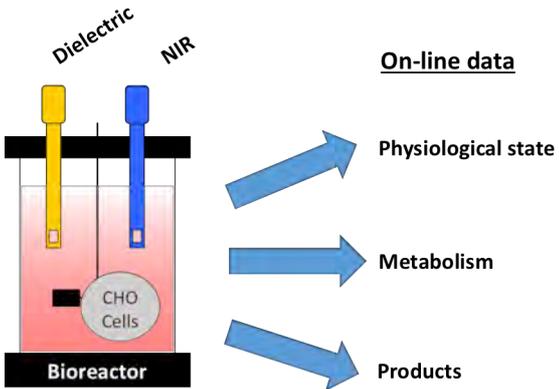
Biological studies (in CRAN, UMR 7039 CNRS-UL):

Uptake, dark cytotoxicity, selectivity phototoxicity, PDT effects

References

- [1]Azaïs et al., *Int J Gynecol Cancer*, under press.
- [2]Verhille et al., *Curr. Med. Chem.*, **2012**.
- [3]Bechet et al., *Cancer Treat. Rev.*, **2014**, PMID: 22858248.

<p>2015</p> 	<p>Online monitoring of animal cells culture processes using various spectroscopic tools</p> <p><u>Franck Courtès (Postdoctoral researcher)</u></p> <p>Annie Marc, Bruno Ebel, Emmanuel Guédon BioProcesses-BioMolecules</p>	
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<p>General context, scientific issues</p> <p>Bioprocesses of mammalian cell culture have become essential in pharmaceutical fields for the production of recombinant therapeutic proteins or for cellular therapy. Consequently, the PAT (Process Analytical Technology) approach recommended by the FDA incites the use of online characterization tools to control production processes and ensure the quality of end-products for patients. In this context, spectroscopic technologies have gained great attention over the past decade as online tools to monitor cellular bioprocesses.</p>	<p>Illustration</p> 
<p>Objectives and stakes</p> <ul style="list-style-type: none"> To cultivate mammalian Chinese Hamster Ovary (CHO) cells in a stirred bioreactor, equipped with NIR (near infrared) and dielectric on-line spectroscopic sensors. To develop chemometric approaches for data processing. To perform online prediction of multiple cultivation variables during bioprocess monitoring. 	<p>Main results</p> <ul style="list-style-type: none"> A multivariate approach was developed to follow cultivation variables during bioprocess monitoring. PLS regression revealed good predictive capabilities to estimate glucose, lactate, glutamine and ammonium contents and, for the first time, LDH activity. Dielectric probe allowed determining the different cellular densities within the VCD and DCD populations in real time with respectively permittivity and conductivity analyses. Lysed cells are generally not accounted for, although they could represent a significant proportion of the cell population in bioreactors. Therefore, they should be considered for optimal control of processes. Dual spectroscopy strategy (NIR combined with dielectric probe) was developed to follow for the first time lysed cells density. Studies with another spectroscopic technology (Raman spectroscopy) are in progress.
<p>Methodology/ Experimental approach</p> <ul style="list-style-type: none"> 10 standard cultures of CHO cells were performed in bioreactor to get the NIR and dielectric calibration models. In order to develop robust models, 5 additional cultures were submitted to environmental variations including temperature shift from 37 °C to 32 °C as well as glucose and/or glutamine feedings. Cell populations (viable (VCD), dead (DVD) and lysed cells), glucose, lactate, ammonium, glutamine and LDH contents have been quantified with off-line methods to allow the models calibration. For treatment of NIR spectral data, a PLS modeling with cross-validation was adopted for the quantitative regression model. Permittivity and conductivity of culture medium were measured online with the dielectric sensor. 	<p>Reference</p> <ul style="list-style-type: none"> F. Courtès, B. Ebel, E. Guedon, A. Marc. Real-time monitoring of the physiological state of CHO cells in bioreactor by using a dual spectroscopic strategy (BMC Proc. 2015)

2015



Development of an intensified process of enzymatic acylation of peptides by multi-scale modeling approach

Dettori Léna (first Year of PhD)

Chevalot Isabelle, Yann Guiavarc'h
BioProMo



General context, scientific issues

Peptides and amino acids can be acylated to produce biosurfactants exhibiting many properties with an application potential as therapeutic, cosmetic and nutraceutical agents. Currently, chemical acylation shows limitations concerning the reaction selectivity and safety in respect to the environment. An alternative to this chemical route is the use of enzymes allowing the catalysis of these 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 to intensify the acylation process based on a more rational approach.

Objectives and stakes

To develop a process for enzymatic acylation of peptides and amino acids by combining experimental and molecular modelling approaches in order to describe the phenomenon at different scales.

Methodology/ Experimental approach

A preliminary study has been performed to develop analytical methods to characterize and quantify acylated molecules.

Different strategies have been developed at different scales for the intensification of acylation bioprocesses:

- at molecular scale: to improve understanding of enzyme/substrates binding modes and predict enzymatic selectivity
- at reaction scale: to study and model reaction kinetics depending on the nature of the biocatalyst and its environment (solvent, aqueous, sCO₂...) [1]
- at process scale: to immobilize enzymes on silica beads [2] in order to recycle them and increase their structural stability

Illustration

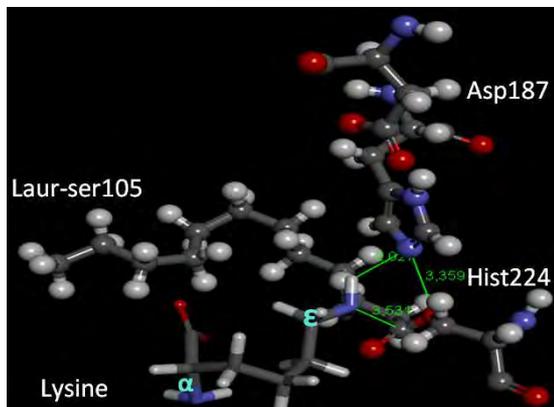


Figure 1: Lysine docking in the active site of lauroyl-lipase (---: distance Å)

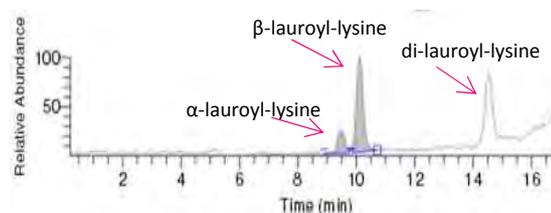


Figure 2: synthesis of lauroyl-lysine using *Candida antarctica* lipase B (mass spectrometry, lauroyl-lysine: m/z = 329)

Main results

- development of analytical methods by HPLC-MS using an innovative C30 column allowing to separate and quantify acylated molecules
- prediction of regio-selectivity of lysine acylation with lauric acid using the *Candida antarctica* lipase B:
 - modelling of enzyme/substrates complexes, suggesting that lysine can be acylated on its both amino groups with the synthesis of two mono-acylated and one di-acylated products (Figure 1)
 - o experimental validation of lysine acylation with lauric acid (Figure2)
- immobilization of acylases mixture from *Streptomyces ambofaciens* on silica beads while preserving their enzymatic activity

References [1]F.Ferrari et al., 2014
[2]J.Jacoby et al., 2013



General context, scientific issues

Succinic acid is a linear and bi-functional molecule that has several applications in food, chemical and pharmaceutical industries. It is mainly produced from fossil resources. Faced to the limited availability of these resources and their impact in global warming, bioprocesses for the production of succinate receive an increased interest. Several anaerobic bacteria naturally produce high concentrations of succinic acid from renewable feedstocks. Moreover, some genetically modified bacterial strains may produce up to 100 g L⁻¹ succinate. Whereas *C. glutamicum* is widely used for the industrial production of amino acids, recent studies revealed the capability of this bacterium to produce several organic acids including succinate.

Objectives and stakes

- Develop an one-step process for the production of succinate using *C. glutamicum*.
- Determine the influence of oxygenation during the transition between growth and production
- Evaluate the robustness of *C. glutamicum* facing to oscillations in dissolved oxygen concentration during the succinate production process.

Methodology/ Experimental approach

This project couples methodologies and approaches from metabolic engineering (gene deletion) and process engineering (process design, scale-down). It can be divided in the five steps described in Figure 1.

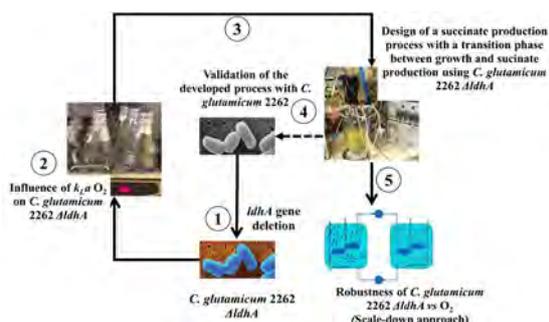


Figure 1: experimental approach of the thesis work

Illustrations



Figure 2: two-compartment scale-down bioreactors system with aerobic and anaerobic bioreactors

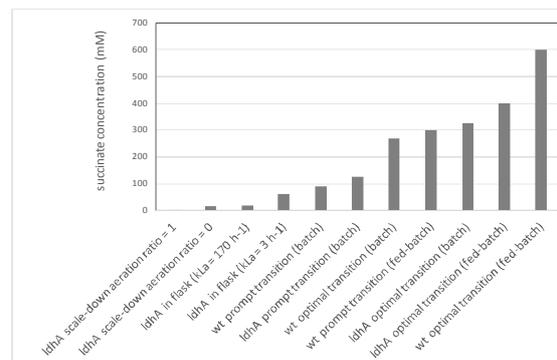


Figure 3: improvement in the succinate production during the PhD project.

Main results

- In flask, $k_L a$ between 10 and 19 h⁻¹ resulted in optimal succinic acid production (63 mM).
- a triphasic process including successively an aerobic, a deoxygenation and an anaerobic phase was designed.
- Up to 327 and 600 mM succinate were produced in batch and fed-batch cultures, respectively.
- The deoxygenation strategy is of key importance in the succinate production process and thus requires the engineering of the bacterium and the process.
- *C. glutamicum* is able to recover very rapidly its oxidative metabolism but not its fermentative one.

Reference

Kaboré A.K. et al, Biochem. Eng. J., 2015, in press

2015



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

Lebranchu Aline (First Year of PhD)

Michel Fick

BioProMo



General context, scientific issues

Anaerobic digestion process needs further development to enhance its economical rentability. Indeed, a biogas plant typically products a mixture of CH₄ (60%) and CO₂ (40 %), indicating possible increase of production yields. One way of improvement consists in injecting H₂ in the digester as archaeobacterial consume H₂ and CO₂ to product CH₄.

Objectives and stakes

To increase the proportion of CH₄ produced. To reach this goal, we must answer to these questions:

- Which design for the bioreactor?
- Is mixing positive to CH₄ production?
- Which technology for H₂ injection?

Methodology/ Experimental approach

The first difficulty is that cattle manure is *a priori* a viscous shear-thinning fluid, raising key issues of bioreactor homogenization. Furthermore agitation is seldom studied in digestors. As helical ribbon are reputed efficient for non-newtonian homogenization, a dedicated vessel equipped with a double helical ribbon was designed and built. To optimize its operation, a rheological characterization of raw, filtered and grinded cattle and also of grinded digestate was first made using a viscosimeter. Using the same set-up and a Newtonian fluid (glycerol), the power curve of the impeller was also established. Secondly, digestate flow behaviour was modelled using a mixture of gum, allowing easier study of gas injection efficiency and gas-liquid mass transfer in our bioreactor.

The second step of this project is to work on the gas dispersion and to study the impact of agitation and hydrogen injection on CH₄ productivity.

Illustration:

Dedicated vessel:



Main results

- The filtration of manure leads to a loss of methanogen power (-50%) because of the loss of valuable solid fraction → it is thus preferable to grind manure instead of filter it.
- Grinded manure viscosity has been modeled using the following law:
$$\mu = 7.9 \cdot \dot{\gamma}^{-0.79}$$
- While grinded digestate viscosity follows :
$$\mu = 4.9 \cdot \dot{\gamma}^{-0.61}$$
- It was also shown that rheological properties evolved during the anaerobic digestion.

The gum mixture modelling the rheology of digestate is a mix of xanthane (5.9 g/L) and guar gums (1.6 g/L) with the rheological law:

$$\mu = 4.4 \cdot \dot{\gamma}^{-0.63}$$

References

- Cheng, Jianya, et Pierre J. Carreau. « Mixing in the transition flow regime with helical ribbon agitators ». *The Canadian Journal of Chemical Engineering* 72, n° 3 (1994): 418-430

<p>2015</p> 	<p>Expansion process of Mesenchymal Stem Cells in stirred bioreactors using 3D microcarriers</p> <p><u>Céline Martin (3rd Year)</u></p> <p>Annie MARC, Éric OLMOS BioProcédés-BioMolécules</p>	
<p>General context, scientific issues</p> <p>Rapid <i>in vitro</i> expansion of Mesenchymal Stem Cells (MSC), isolated from biopsies, is a key step for their use in cell therapies or tissue engineering. To reach the required amount of cells (several hundred million of cells/dose), 3D culture in bioreactors with cells adhered on spheric microcarriers could be an alternative to classical 2D culture, provided that their properties of differentiation are preserved.</p>		<p>Illustration</p>  <p><i>Parallel stirred mini-bioreactors controlled with pH, dissolved O₂ and temperature sensors, used for MSC expansion in 3D culture system</i></p>
<p>Objectives and stakes</p> <p>We aimed at studying process intensification of the expansion of human bone marrow MSC on microcarriers, using stirred-tank bioreactors:</p> <ul style="list-style-type: none"> • study of the impact of microcarriers ($\phi = 200 \mu\text{m}$) suspension and agitation on MSC growth and properties; • fully MSC characterization via biological assays throughout the process; • removal of calf serum from culture medium to streamline and secure the expansion process. 		<p>Main results</p> <ul style="list-style-type: none"> • MSC must be more investigated in order to become a cell model reliable enough to develop a robust expansion process. • One of microcarriers crucial characteristics is their ability to release the cells when they are due to be harvested or analyzed and not only their ability to support cell proliferation. • Stirred-tank bioreactors for the expansion of MSC on microcarriers must be carefully regulated (temperature, agitation...), in order to limit cell growth stop and death. • Nutritional needs of MSC are complex since addition of dozen of growth factors partially replace serum for MSC expansion on microcarriers, or in 2D. • Critical agitation parameters for microcarriers suspension have also been studied in the case of orbital shaken bioreactors.
<p>Methodology/ Experimental approach</p> <ul style="list-style-type: none"> • The freezing method for MSC banking in liquid nitrogen was improved to get enough biological material. • Various batch cultures were performed in small-scale bioreactors (200 mL), using 3 types of impellers (Rushton, marine Impeller, and Elephant Ears). • Operating parameters that impact microcarrier suspension (turbulent dissipation rate, impeller design, [carrier]) were studied through an experimental design. • A DoE was also used to substitute calf serum by a mix of different cell growth factors. • Numerous methods were set up to characterize the MSC (morphology, viability, growth, stemness, adhesion...). 		<p>Reference</p> <ul style="list-style-type: none"> • Olmos, E., Loubière, K., Martin, C., Delaplace, G., Marc, A. Critical agitation for microcarrier suspension in orbital shaken bioreactors: experimental study and dimensional analysis. <i>Chemical Engineering Science</i>. 122, 545-554 (2015)

2015



Synthesis of new systems based on photosensitizers for the improvement of the tumor selectivity in photodynamic therapy

STALLIVIERI Aurélie (Third Year of PhD)
Céline FROCHOT
Isabelle CHEVALOT
Biopromo



General context, scientific issues

Photodynamic therapy (PDT) is a therapeutic cancer treatment based on the combination of light, oxygen and a photosensitizer (PS). The action of light on the PS in the presence of oxygen leads to the formation of reactive oxygen species, including singlet oxygen 1O_2 , leading to necrosis or apoptosis of cancer cells. One limitation of photodynamic therapy is the low selectivity of PS to tumour tissue. The design of new PS more selective focus on the synthesis of i) PS coupled with substrate specific of the membrane receptors overexpressed in certain cancers; ii) PS being active only in tumoral zones, called photomolecular beacon.

Objectives and stakes

Synthesis of a new generation of more selective photosensitizers:

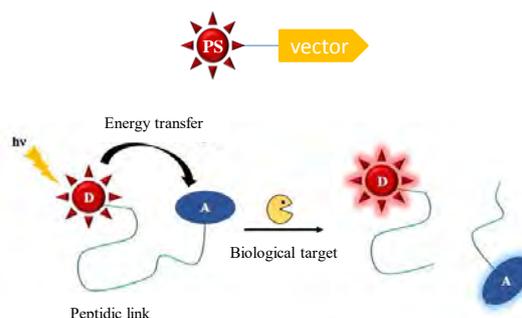
- increase the selectivity of PS for cancer cells,
- control the production of singlet oxygen in cancer tissues.

Methodology/ Experimental approach

A first approach considered in this thesis is to modify PS by coupling them to vectors with high affinity for specific membrane receptors of tumor cells.

The second approach developed in this work was to control the production of singlet oxygen only when the PS has reached the target using the action of specific enzymes in the tumor area.

Illustration



Main results

- PS conjugated to folic acid present higher affinity for folic acid receptor than non targeted PS and good photophysical properties (high singlet oxygen quantum yield).
- PS coupled with a peptide targeting neuropilin-1 presents higher affinity for neuropilin-1 receptor than peptide alone and good photophysical properties.
- Different photodynamic molecular beacons (PMB), composed of a photosensitizer and a quencher linked together by a peptide substrate of MMP-2, MMP-9 and MMP-14, have been synthesized. The quantity of cleavage depends mainly on the type of the photosensitizer.
- The development of alternative synthesis with enzyme such as the lipase B of *Candida antarctica* allowed the conjugation of lysine (present on the peptide substrate) with the quencher.

References

- Stallivieri, A.; Baros, F.; Jetpisbayeva, G.; Myrzakhmetov, B.; Frochot, C.; *The interest of folic acid in targeted photodynamic therapy*: submitted in *Curr. Med. Chem.* **2015**.
- Azaïs, H.; Schmitt, C.; Tardivel, M.; Kerdraon, O.; Stallivieri, A.; Frochot, C.; Betrouni, N.; Collinet, P.; Mordon, S.; *Treating peritoneal micrometastasis by targeted photodynamic therapy to decrease peritoneal recurrence rate after complete cytoreductive surgery in epithelial ovarian cancer. Specificity of a new generation folate-targeted photosensitizer. A preclinical study*: submitted in *Gynecol. Oncol.* **2015**.
- Stallivieri A., Baros F., Arnoux P., Vanderesse R., Barberi-Heyob M., Frochot C. *Production of singlet oxygen by nanoparticle-bound photosensitizers*, Singlet Oxygen: Applications in Biosciences and Nanosciences edited by Santi Nonell and Cristina Flors **2015**.

2015



Carotenoids Extraction from Peach, kaki and Apricot fruits and their potential as singlet oxygen quenchers

Khalil ZAGHDOUDI (PHD)

Céline Frochot - Régis Vanderesse - Yann Guiavarc'h
BioProMo- LCPM



General context & scientific issues

Carotenoids are lipid soluble pigments produced as secondary metabolites in fruits, vegetables, algae, fungi and some bacteria. Such pigments are involved in the prevention of several diseases such as cancer, age-related macular degeneration and other disease related to immune function [1]. However carotenoids are well-known in nature for their role in quenching excited states of photosensitizers and in directly scavenging $^1\text{O}_2$. Over the last 50 years many efforts were put on the development of improved carotenoids extraction through various analytical methods [2] Accelerated solvent extraction presents interesting features but, in the last 10 years only few research papers using ASE technique for carotenoids extraction were published.

Objectives and stakes

- Better control & understanding of carotenoids extraction parameters with ASE process
- Maximizing carotenoids extraction yields of the four main carotenoids targeted in three fruits (kaki, peach, apricot).
- Modeling & optimization of carotenoids extraction parameters with ASE process
- Identification & quantification of the major pigments of in the three fruits
- Evaluation of $^1\text{O}_2$ quenching by carotenoids

Methodology/ Experimental approach

Extraction:

Extraction experiments of 2 g of each fruit powder with known particle size and water activity were carried out in static mode with Dionex ASE 350 extractor. Solvent (MeOH/THF) was set to 20, 60 & 100 % MeOH, temperature was set to 40, 60 & 80°C. Pressure was kept constant (103 bar).

Experimental design:

A two factors-two levels full factorial design with additional central point was carried with JMP 10 software from SAS Institute Inc (Cary, NC, USA).

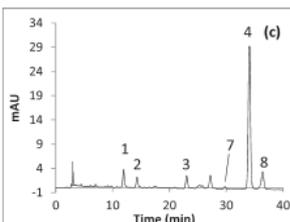
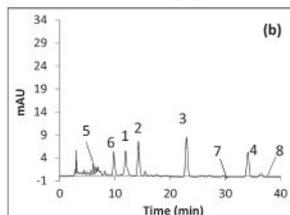
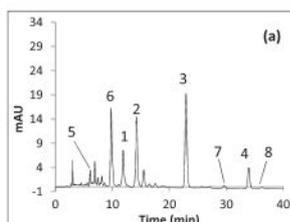
Characterization techniques:

HPLC-PDA, LC-MS (C30 YMC column, (MeOH/MTBE) gradient as mobile phase).

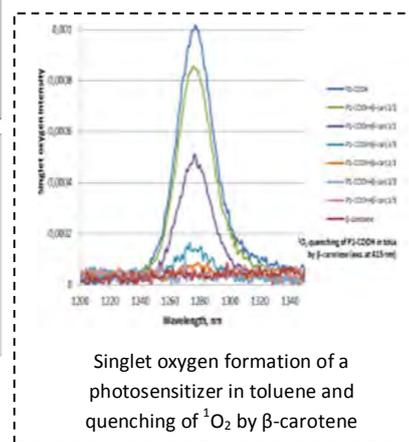
Photo-physical characterization:

UV-visible absorption/Fluorescence Emission/ Singlet Oxygen Quenching.

Illustration: Carotenoids profile using ASE optimal separation conditions (a): Kaki, (b): Peach, (c): Apricot



- (1): all-trans-lutein
- (2): all trans-zeaxanthin
- (3): all-trans- β -cryptoxanthin
- (4): all-trans- β -carotene
- (5): all-trans-neoxanthin
- (6): all-trans-violaxanthin
- (7): 13-cis- β -carotene
- (8): 9-cis- β -carotene



Singlet oxygen formation of a photosensitizer in toluene and quenching of $^1\text{O}_2$ by β -carotene

Main results

- Accelerated Solvent Extraction proved to be an efficient technique for carotenoids extraction from fruits matrix [3].
- The generated model gave significant R^2 -values with normally distributed residuals.
- Optimal conditions were found for the four identified carotenoids.
- The characterization of the major carotenoids were achieved & additional carotenoids were identified with LC-MS.
- $^1\text{O}_2$ quenching properties of the four targeted carotenoids were evaluated.
- Separation & purification of major carotenoids were performed using preparative chromatography.
- We also used supercritical fluid extraction (SFE) process with supercritical CO_2 as main solvent and ethanol as co-solvent; The influence of five extraction factors were evaluated using surfaces responses methodology (5 factors and three levels per factor); Predictive models were set-up and comparison between the extraction techniques were established.

References

- [1]:Peirera et al., *IJFP*.(2007).
[2]:Amorim-Carrilho et al., *Trends in Analytical Chemistry*. (2014)
[3]:Zaghdoudi et al., *Food Chemistry*. (2015)

2015



TiO₂ nanoparticles coupled to photosensitizers for applications in photocatalysis and photodynamic therapy

Zahraa YOUSSEF (1st year)

Thibault Roques-Carmes – Céline Frochot
Prism – BioProMo



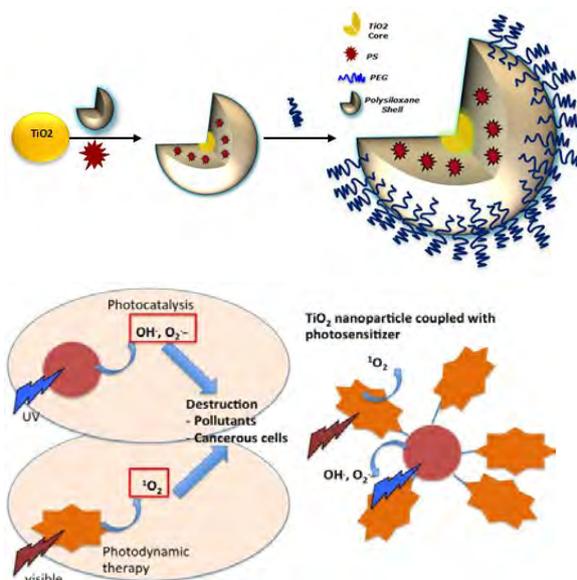
General context, scientific issues

Photocatalytic degradation is an alternative method for the removal of environmental pollutants in aqueous phase. The photochemical technology using TiO₂ photocatalyst for the water treatment process is known as a clean method [1].

Photodynamic therapy is a promising substitute treatment approach against cancer. The efficacy of PDT depends on the photosensitizer's ability to produce ROS and ¹O₂, oxygen availability, light dose and photosensitizer concentration in the treated area [2].

Photocatalysis with TiO₂ suffers from its large band gap energy, UV-limited photoresponse and fast recombination rate of the photogenerated electron-hole pairs. Also PDT suffers from selectivity. Synthesis of functionalized nanoparticles may circumvent all these drawbacks and would elaborate new nanoparticles that could be used for these two different kind of applications.

Illustration:



Objectives and stakes

Grafting visible light sensitive photosensitizers onto the surface of titania would enable us to:

- Produce different types of ROS that would potentially lead to an increase of the photodynamic and photocatalytic efficiencies,
- Optimize the number of grafted PS to lead to the best photodynamic and photocatalytic efficiencies,
- Address, through suitable surface modifications (e.g. PEG grafting and peptides), nanoparticles for tumor-specific receptors.

Methodology/ Experimental approach

•Sol-Gel Synthesis:

- PS to be used: monocarboxylic tetraphenylporphyrin (activated, LRGP), Chlorin e6, PPIX, phthalocyanine.
- Preparation of hybrid TiO₂/APTES/TEOS/PS/PEG NP (LRGP in collaboration with LCPML-Lyon) [3]:
 1. Dispersion of TiO₂ nanoparticles in DEG
 2. Encapsulation of the TiO₂ core in polysiloxane shell formed from APTES and TEOS
 3. Grafting of the activated PS onto the surface of TiO₂
 4. Grafting of hydrophilic PEG onto the hybrid TiO₂ NP

•Characterization techniques:

Zeta potential, DLS, FTIR, TOC, UV-visible absorption, fluorescence emission, ROS detection, TEM

•Stability experiments TiO₂/APTES/TEOS/PS/PEG : photostability, dispersion in solution, reusability, etc

•Application in PDT and Photocatalysis

Main results

- Since TiO₂ nanoparticles exhibit a massive aggregation, we have tested its dispersion in several solvents such as: DEG, 90%DEG-10%Ethanol, 50%DEG-50%Ethanol, Ethanol and 90%Cyclohexane-10%Ethanol. Stable dispersion of TiO₂ nanoparticles in DEG is attained.

- We prepared and purified hybrid TiO₂ nanoparticles surrounded by a polysiloxane shell. Several characterization techniques such as DLS, TEM and zeta potential were performed on these NP.

- Different types and amounts of PS will be grafted onto the encapsulated TiO₂ nanoparticles and then characterized by various techniques.

- The Photodynamic and Photocatalytic efficiency of the prepared catalyst will be estimated in solution and *in vitro*.

References

- [1] Zimny et al., J. Phy. Chem. C, 2012, p. 6585-6594
 [2] Bechet et al., Trends in biotech., 2008, p. 612-621
 [3] Couleaud et al., Nanomedicine, 2011, p. 995-1009

Kinetics And Thermodynamics For Energy And Products



LABORATOIRE
REACTIONS AND



REACTIONS ET GENIE DES PROCEDES
CHEMICAL ENGINEERING LABORATORY



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 into high temperature and high pressure reservoirs, some of them associated with H₂S and sulfur compounds.

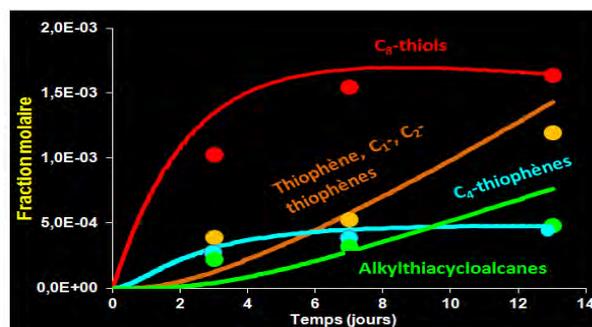
In order to make these kind of oils environmentally and economically profitable it is necessary to improve the current exploration tools based on the understanding of hydrocarbons geochemistry to guarantee the quality, phase and amount of the resources that are going to be extracted.

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.

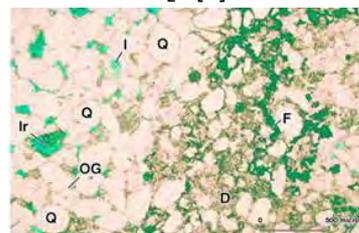
Objectives and stakes

- 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 H₂S role.
- Integrating reduced kinetic models into COMSOL Multiphysics to improve accuracy of oil reservoir simulations.
- Considering the reinjection of H₂S into depleted oil reservoir as a strategy of environmental treatment of acid gases produced during extraction and refining of hydrocarbons.

Illustration



Previous reactivity studies: Alkanes (n-octane) with H₂S [2]



Flow of oil after steam injection in a reservoir

Methodology/ Experimental approach

Confined pyrolysis under high pressure (700 bar) and temperature (300°C - 400°C): The sample mixture (aromatic, H₂S) is introduced and sealed into a gold tube which is heated into an autoclave. The reaction time is set from 24 hours to 13 days and varies with the temperature to simulate the geological maturation age of the reservoir. The products will be analyzed using coupled Gas chromatography mass spectrometry (GC-MS), Gas chromatography – Flame photometry detector (GC-FPD), gas chromatography - Flame ionization Detector (GC-FID) [1, 2].

Kinetic modelling: a detailed kinetic model will be constructed based on free-radical chemistry.

References

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- [2] **Pyrolysis mechanism of the n-octane/H₂S mixture at 70 MPa and 603–623 K.** V. P. Nguyen, V. Burklé-Vitzthum, P.M. Marquaire, R. Michels. *Journal of Analytical and Applied Pyrolysis*. 2014. doi :10.1016/j.jaap.2014.09.025



Thermal evolution of HP/HT fluids in reservoirs Pyrolysis of alkylcycloalkanes

Darwin A. Rakotoalimanana (3rd year)

¹Paul-Marie Marquaire, ¹Roda Bounaceur, ²Françoise Béhar
¹LRPG, CRT – ²TOTAL E&P



General context, scientific issues

The thermal evolution of petroleum in reservoirs over the last geologic periods is controlled by the kinetics of thermal cracking. High temperature/High pressure (HP/HT) fluids, which have become new assets in our resources, correspond to the petroleum contained in Deeply Buried Reservoirs (5000-6000 m depth) such as Elgin reservoir in North Sea where temperature and pressure are greater than 170°C and 700 bar respectively. They show a higher content of alkylcycloalkanes, also known as naphthenes (usually more than 30 wt %). Yet until now, very few studies on naphthenes at high pressure and low temperature have been done unlike the case of alkanes or more recently aromatic compounds [1-2].

Objectives and stakes

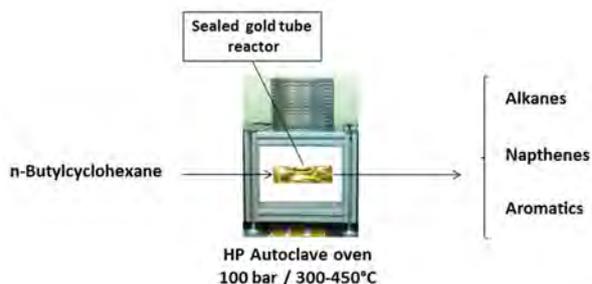
The objective of this work is to understand the thermal cracking of naphthenes at geological conditions (100-1000 bars, 150-220°C). In the meantime, this study contributes to the development of a global model [3-4] which enables to predict the composition and the thermal evolution of oils in reservoirs and by extent their economic interest in current oil exploration.

Methodology/ Experimental approach

As petroleum constitutes a complex chemical mixture, each chemical class was studied firstly apart via a model compound. In our case for naphtene, n-butylcyclohexane $C_{10}H_{20}$ (BCH) was chosen to also take into account the effect of the side alkyl chain. The pyrolysis of BCH in sealed gold tube reactor was studied at 100 bar and 300-425°C during 9-672 h in pure conditions and in mixture with n-octane, whose thermal cracking is well-known. A kinetic model based on free-radical mechanism [5] will describe our experimental results and enable to simulate the reactivity of naphthenes in reservoirs by extrapolating the temperature.

Illustration

Gold sealed tube reactor is placed in an HP autoclave oven and heated at a temperature and a pressure (both kept constant) for a given time



Main results

The conversion of n-butylcyclohexane in our conditions was between 3 and 99%: it starts to be significant (>20%) at 400°C after 24h. The pyrolysis of BCH mainly leads to the formation of three chemical classes: n-alkanes (mainly C_1-C_3), naphthenes (mainly cyclohexane and methylcyclohexane) and aromatic compounds (benzene, toluene and butylbenzene). Possible reaction pathways were formulated to explain the formation of the main products such as C-C breakings, aromatization and cycle contraction among others. Several comparisons with other model compound of other chemical class highlight that the longer the alkyl side chain, the faster the conversion is. At equivalent carbon number, a naphtene has the same behavior as n-alkane but is more stable than the alkylated aromatic equivalent. Additional experimental data was also gathered to observe the effect of the number of cycle by studying the n-butyldecalin $C_{14}H_{26}$.

References

- [1] Lannuzel et al., JAAP., 2010, p 236-247
- [2] Fusetti et al., Org. Geochem., 2010, p 146-167
- [3] Dominé et al, Org. Geochem., 2002, p 1487-1499
- [3] Behar et al., Org. Geochem., 2008, p 764-782
- [4] Bounaceur et al., JAAP, 2013, p 240-254

2015



Thermal decomposition of Jetfuels for hypersonic flights

Audrey Tritz (Post doc MBDA)

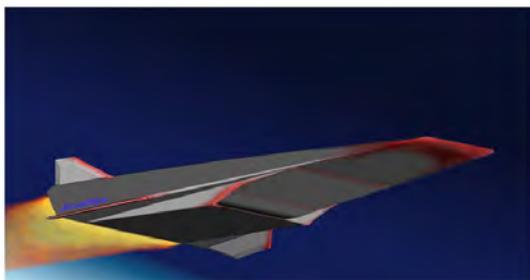
Paul-Marie Marquaire, Yves Simon

CRT



General context, scientific issues

Hypersonic researches are focusing on the thermal management of the vehicle and more especially of the engine because of the large heat load due to the high velocity and the combustion of the fuel. One method, called active cooling or regenerative cooling, consists in using the fuel heat sink capability due to the endothermicity of its thermal decomposition. Especially at high Mach numbers (5-10), fuel is an attractive heat sink. Jetfuels used in aeronautic are mainly petroleum based kerosenes containing several classes of hydrocarbons. Other jetfuels are pure hydrocarbons or mixtures containing molecules such as n-dodecane or tricyclodecane. In the literature, there is a significant lack of experimental data about cyclane pyrolysis. In order to better understand the thermal decomposition of jetfuels, different model molecules are studied.



Objectives and stakes

- Study of the thermal decomposition of a jetfuel
- Study of the pyrolysis of model molecules : n-dodecane, iso-dodecane, methylcyclohexane
- Improving a detailed kinetic mechanism based on elementary steps and validated with experimental data

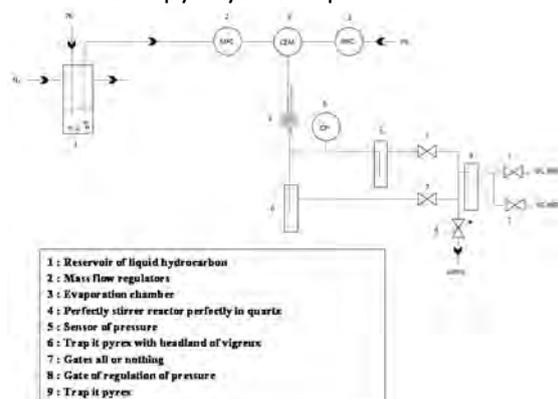
Methodology/ Experimental approach

Pyrolysis is studied in a continuous perfectly stirred reactor, for an initial mole fraction of 3 % diluted in helium, at atmospheric pressure. The residence time is 1s, whereas the temperature ranges from 500°C to 800°C. Several intermediate species are formed during pyrolysis and have been identified by GC/MS and quantified by GC/FID.

The quantification of light (i.e. $< C_5$) products of pyrolysis is performed on line with gas phase chromatograph using FID and TCD detectors.

Heavy (i.e. $> C_5$) products of pyrolysis are condensed at the outlet of the reactor in a cooled trap with liquid nitrogen during ten minutes. They are then dissolved in acetone to be analyzed on a gas phase chromatograph using FID detector.

Illustration : pyrolysis setup



Main results

- The pyrolysis of a jetfuel and n-dodecane, iso-dodecane, methylcyclohexane are studied between 500 to 800°C.
- For the same range of temperature, the conversion is more important in the case of iso-dodecane (10% to 100%) than n-dodecane (2% to 70%) and methylcyclohexane (0% to 55%).
- The main products of the pyrolysis reaction are the same for the three compounds and the jetfuel. They are hydrogen, methane, ethylene, propylene, benzene, toluene and cyclohexene, but the distributions of products are different.
- The pyrolysis of a surrogate mixture of 3 model molecules is equivalent to the jet-fuel pyrolysis.
- All these new experimental data are used to improve this detailed kinetic mechanism of pyrolysis based on elementary steps.
- The kinetic model of pyrolysis allows to quantify the heat transfer and the composition of the mixture entering into the combustion chamber.

References

- Dahm et al, JAAP, 2004, p 865-881
- Edwards, CST 2006, p 307-334
- Herbinet et al, JAAP, 2007, p 419-429
- Bounaceur et al, JAAP, 2013, p 240-254

2015



Investigation of biomass pyrolysis by photoionization mass spectrometry (PI-MS)

Jia Liangyuan (Post-doctor)

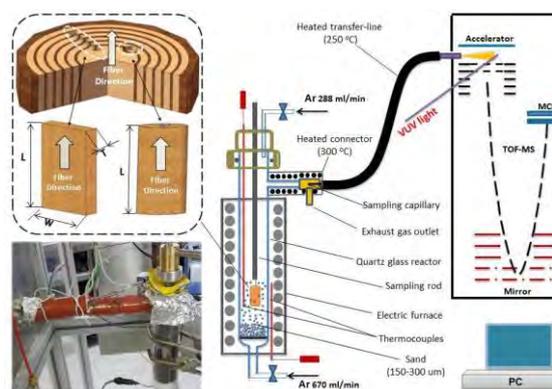
Supervisor: Anthony Dufour
Greener



General context, scientific issues

- Pyrolysis is one of the main methods for conversion of biomass to clean fuels and chemicals. It is required to obtain detailed information on pyrolysis products distribution and on the chemical kinetics.
- PI-MS is a soft and accurate method for on-line analysis of pyrolysis vapours.
- On-line investigation by PI-MS is more likely to get real information on processes and mechanism of biomass pyrolysis

Illustration (result, methodology or context)



PI-MS combined with fluidized-bed reactor

Objectives and stakes

- PI-MS have to be successfully combined to different reactors with a hot sampling line to obtain accurate and reproducible results.
- To understand the mass and heat transfers during biomass pyrolysis by the on-line PIMS analysis
- The major difficulty is that several proper interfaces between PI-MS and different reactors have to be designed.

Main results

- PI-MS has been successfully combined to fixed-bed and fluidized-bed reactors, and the results demonstrate it is really fast and versatile to investigate biomass pyrolysis due to its soft ionization method and on-line analysis
- Different types of products were formed at different temperatures and different stages of biomass pyrolysis
- Wood particles size shows a significant influence on conversion time and products distribution because of different mass and heat transfers effects
- Experimental results are currently compared with detailed models from literature

Methodology/ Experimental approach

- Combination of PI-MS and fixed-bed reactor to investigate the slow pyrolysis of different biomass powders
- Combination of PI-MS and fluidized-bed reactor to investigate the fast pyrolysis of powder and thermally-thick wood particles
- Combination of PI-MS, IR-imaging and laser-heating device to investigate the formation of primary products and bio-char
- Combination of experimental results and kinetic models to simulate the mechanism of biomass pyrolysis

References

- 1) Jia, L. Y. et al. Effect of biomass particle size and shape on the primary products from fast pyrolysis in a micro-fluidised bed 2015 (in preparation)
- 2) Dufour, A et al. *Rsc Advances* 2013, 3(14), 4786-4792
- 3) Fendt, A et al. *Energy & Fuels* 2012, 26(1), 701-711

2015



Modeling of a biomass thermochemical conversion process

Maione, Riccardo (second year of PhD)

Supervisors : G. Mauviel and G. Wild

Name of your department (axis) Reactions and Reactors



General context, scientific issues

Energy production and sustainable heat from thermochemical biomass conversion are at the center of scientific and industrial interest due to lower availability of fossil fuels and pollution produced by their combustion. Process modeling can come to aid reducing costs and time spent for research. In this PhD, a pyro-gasification process of wood biomass consisting of 3 separated reactors will be modeled. In this system, every step of reaction (namely pyrolysis, char partial oxidation and gasification) are done in different reactors. Steel balls are used mostly as heat vector transferring the heat produced by char oxidation into the pyrolysis reactor. In order to improve the heat transfer and the dynamic transport, all the reactors are rotating.

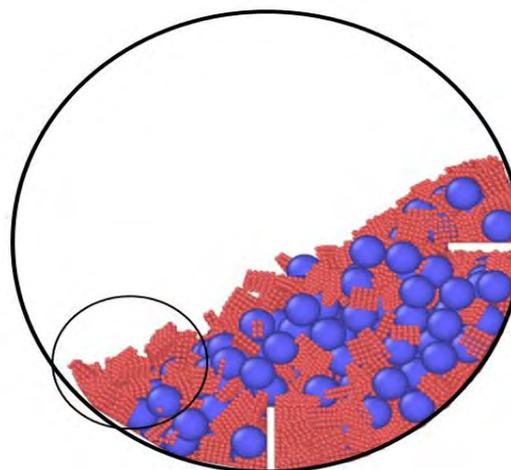
Objectives and stakes

- Extrapolate a model of the pyro-gasification process
- Optimize the SEA Marconi process

Methodology/ Experimental approach

The modeling of 3 reactors will be done by coupling different codes that perform specific functions. The main code is LIGGGHTS: this discrete element method (DEM) code resolve the equation of motion of the solid phase through rigorous modeling of the contact. Different codes can be coupled to LIGGGHTS in order to get the best suited model for the reactor considered. The models will be validated by means of experimental tests.

Illustration (result, methodology or context)



Bed profile, 5 rpm blue spheres are steel, red particles are wood.

Main results

- Baffles influence on the behavior of a rotating cylinder
- Characterization of particle shape importance in granular modeling of rotating cylinders
- Modeling of reactor dynamics
- Conception of a compressible gas solid reactive system modeling through CFD-DEM coupling and validation of the CFD-DEM solver solving algorithm through comparison with Ergun Equation

References

- P.A. Cundall, O.D. Strack, A discrete numerical model for granular assemblies.
- M. Oevermann, S. Gerber, F. Behrendt, Euler–Lagrange/DEM simulation of wood gasification in a bubbling fluidized bed reactor

2015



Environmental and socio-economic analysis of bioenergy production chains

Pelletier Chloé (2nd year of PhD)

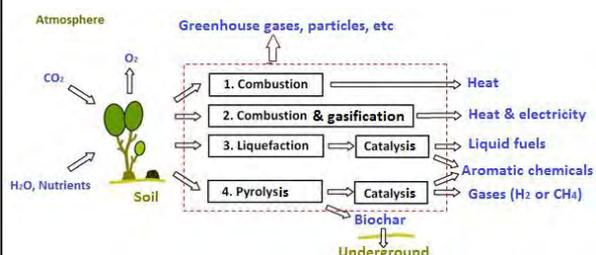
Dufour Anthony, Pons Marie-Noëlle
Axe Réactions et Réacteurs. GREENER group



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

Illustration



Objectives and stakes

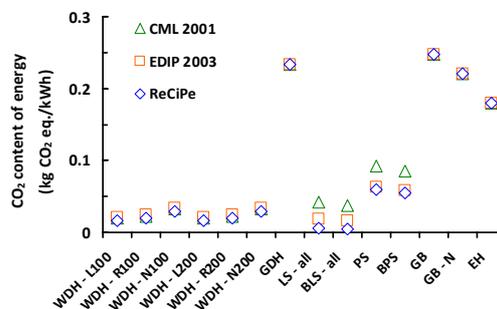
- Establish the Carbon, Oxygen, Hydrogen balance of the different production chains
- Do a Life Cycle Analysis and an economic analysis to compare the different scenarios

Main results

- 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, and is also cheaper for the final user. These results are in need of consolidation.
- We have also seen that the quality of combustion matters greatly, because some minor pollutants have a high Global Warming Potential impact, much higher than CO₂. There is also more uncertainty on these species' GWP according to the LCIA method.

Methodology/ Experimental approach

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



References

J. François, J., M. Fortin, F. Patisson, et A. Dufour. 2014. *Enviro. Sc. & Techno.* 48 (23): 14007-15. doi:10.1021/es5032823.
C. Pelletier, J. François, L. Dieckhoff, M. Fortin, Y. Rogaume, M.-N. Pons, A. Dufour. 2015. Presented at the ECOS2015 conference.

2015



Valorization of lignin to fuels and chemicals

Binod SHRESTHA (3rd year)

Anthony DUFOUR, Sandrine HOPPE, Dimitrios MEIMAROGLOU

Processes for Products and Materials



General context, scientific issues

Lignin is one of the component with aromatic moieties in biomass feedstock. The interest in lignin valorization has been increased due to the socio-economic, environmental and health impact put by the fossil fuel resources. Lignin could be an important resource in fuels and green aromatic chemicals (building blocks). The in-depth understandings of the thermo chemical conversion of lignin by pyrolysis, solvolysis, extrusion, catalysis (etc.) could assist in setting up the industrial way of

Objectives and stakes

The objective of the PhD thesis is to study the different approaches of lignin valorisation which includes pyrolysis, solvolysis (liquefaction), catalytic solvolysis, and twin screw extrusion.

Methodology/ Experimental approach

Lignin pyrolysis was conducted in a rheometer to study the softening and solidification behavior complemented with the chemical transformations.

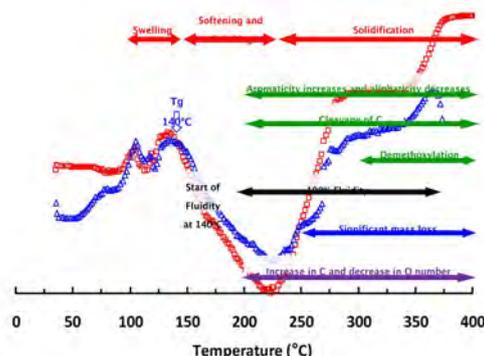
Lignin liquefaction has been performed in Parr instrument 300 mL reactor with high temperature and pressure conditions.

Twin screw extrusion of lignin has been accomplished in a twin screw extruder 'Process 11' from Thermo Scientific.

Catalytic lignin liquefaction will be carried out in the autoclave (150Bar H₂ pressure) with the use of catalysts.

The lignin derived products will be characterized with a wide range of techniques (chromatography, mass spectrometry, UV, SAXS, DLS, NMR, rheology, etc.) to better understand the nature of lignin conversion.

Illustration (result, methodology or context)



Mechanisms of lignin pyrolysis [1]

Main results

- Softening and solidification of lignin pyrolysis along with the chemical transformations.
- Solvolysis products analysis depicts the understanding of lignin degradation.
- Twin screw extrusion of lignin at considered extrusion conditions has been found to be a starting step for further utilisation of lignin, as it enables the melt pumping of lignin without significant degradation.
- Work on catalytic lignin liquefaction is currently performed.

References

- [1] Shrestha et al. 2014, Mechanism of lignin pyrolysis as investigated by in-situ rheology and ex-situ spectroscopic methods, Pyro 2014, May 19-23, Birmingham.

<p>2015</p> 	<p align="center">Study of a treatment “at the root” for reducing Polycyclic Aromatic Hydrocarbons in pyrolysis ovens</p> <p align="center">BENSABATH Tsilla (2nd year of PhD)</p> <p align="center">P.-A. GLAUDE (LRGP); H. MONNIER (INRS) KinCom (axis 4)</p>	
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General context, scientific issues

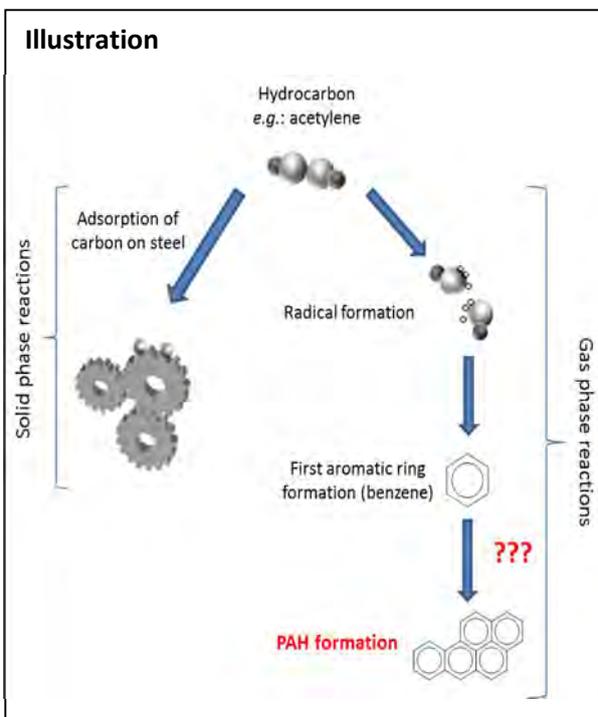
Low-pressure gas carburizing is a heat treatment process used to harden surface steel by enriching the metal with carbon atoms coming from pyrolysis of hydrocarbons. Unfortunately, at the same time, reactions take place in the gas phase and lead to the formation of Polycyclic Aromatic Hydrocarbons (PAHs), precursors of soot. PAHs are toxic to humans and hazardous to the environment. Some of them, like benzo(a)pyrene (C₂₀H₁₂), are known carcinogens.

- Objectives**
- Modeling of the reaction pathways for PAH formation
 - Experimental quantification of PAHs during acetylene pyrolysis
 - Process optimization to limit toxic PAH formation in low-pressure gas carburizing conditions
- Stake**
- Reduction of carcinogen soot formation in pipes at the outlet of carburizing ovens

Methodology/ Experimental approach

The construction of the model is based on a combustion model for hydrocarbons having up to six carbon atoms and which describes the formation of the PAHs up to pyrene (four aromatic rings) [1]. It was modified to adapt it to our conditions (pyrolysis, low pressure...), and completed to take into account heavier PAHs from other models of the literature [2].

For the experimental part, acetylene will be pyrolysed into two reactors: a CSTR and a plug-flow, with different conditions of temperature, pressure and residence time. Products will be determined and quantified by different analysis methods like gas chromatography.



- Main results**
- Model describing PAH formation up to seven aromatic rings (coronene)
 - Focus on sixteen toxic PAHs including benzo(a)pyrene
 - Good orders of magnitude for PAHs in comparison with experimental results from the literature
- Afterward, we will have experimental results in different operating conditions. They will be used to improve the model and, coupled with simulation results, they will serve to optimize the process.

References

[1] M. Nowakowska, O. Herbinet, A. Dufour, P.-A. Glaude, *Combust. Flame* 161 (2014) 1474-1488

[2] K. Norinaga, O. Deutschmann, N. Saegusa, J. Hayashi, *J. Anal. Appl. Pyrolysis* 86 (2009) 148-160

2015



Chemical mechanism of biomass pyrolysis

LE BRECH, Yann (4th)

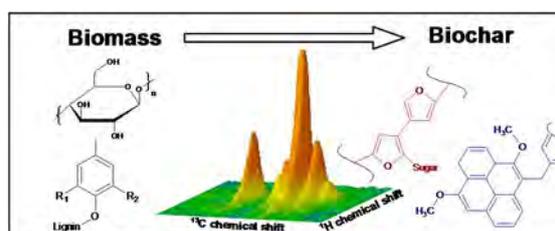
BROSSE Nicolas (Pr UL/LERMAB)
 DUFOUR Anthony (CR CNRS/LRGP)
 Réactions et réacteurs (axe 4)



General context, scientific issues

Biomass is the renewable resource with the highest potential for energy and chemicals production. Current research work focuses on biomass thermochemical conversion. Pyrolysis is the first fundamental mechanism occurring in all thermochemical processes for solid fuels conversion. The aim of this project is thus to develop new methodologies to improve the understanding of the chemical mechanisms of biomass pyrolysis.

Analysis by high resolution ^1H - ^{13}C solid state NMR has revealed the chemical composition of biomass and biochar [1].



Objectives and stakes

- Chemical characterization of products from biomass pyrolysis (char, condensable and gas).
- Investigations on the effect of biomass composition on product composition

Main results

- Characterizations by High Resolution NMR ^{13}C and ^1H - ^{13}C analyses of char structures from biomass slow pyrolysis. The ^1H - ^{13}C characterization have been made on a high field spectrometer (750MHz) with a specific technic (FSLG) [1],
- Characterization of the potassium influence on biomass pyrolysis by combining several analytical methods (calorimetry, thermogravimetry, high temperature in-situ ^1H NMR [2], size-exclusion chromatography coupled with mass spectrometry),
- Investigations on the chemical compositions of volatiles by connecting on the fixed bed reactor an original mass spectrometer with soft ionization (photo-ionisation-TOFMS boughtby LRGP from Photonion company)

Methodology/ Experimental approach

An original fixed bed reactor was used to produce biochar, volatiles and gases from biomass slow pyrolysis. This reactor enables a good control of heat and mass transfer conditions. Miscanthus x Giganteus which is a high potential energy crops was selected for this study. Other biomasses (oak, douglas) and extracted cellulose and lignin were also studied. A global characterization of the pyrolysis products was conducted. Various analytical characterizations (High resolution NMR, Infrared, Calorimetry, Thermogravimetry, gas and liquid chromatography) have been developed to fully characterized char, condensables (tar) and gas.

References

- [1] Le Brech, Y.; Delmotte, L.; Raya, J.; Brosse, N.; Gadiou, R.; Dufour, A., *Anal. Chem.* **2015**, 87 (2), 843–847.
 [2] Dufour, A.; Castro-Diaz, M.; Brosse, N.; Bouroukba, M.; Snape, C. *ChemSusChem* **2012**, 5 (7), 1258–1265.
 [3] Evans, R. J.; Milne, T. A. *Energy Fuels* **1987**, 1 (2), 123–137.

2015



Thermal degradation of toxics

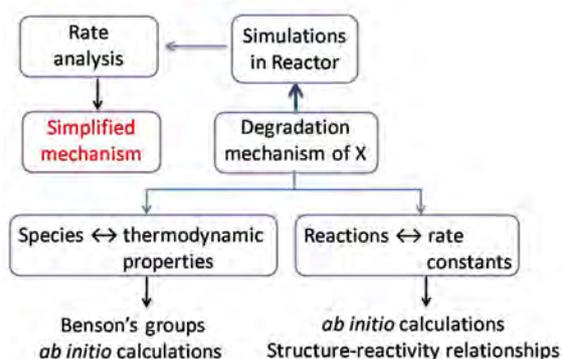
LIZARDO HUERTA, Juan Carlos (Post-doc)

B. Sirjean, R. Fournet and P.A. Glaude
Combustion Kinetics (KinCom)

General context, scientific issues

In partnership with the Centre d'Etude du Bouchet of the Délégation Générale de l'Armement (DGA), we conduct exploratory research in the field of thermodynamic and kinetic mechanistic studies, concerning the development of kinetics models of the degradation of toxic chemical agents, under conditions of high temperatures and high pressure.

Methodology



Objectives and stakes

- Evaluate the physical and chemical properties.
- Provide mechanistic details of the thermal degradation of toxic chemical agents.

Methodology

Study of reaction pathways, rate constants and thermodynamic data of species involved in the degradation processes.

Perform numerical simulations to compare the relative reactivity of chemicals and analyze their reaction pathways to derive simplified mechanisms.

Main results

- Detailed kinetic mechanism of thermal decomposition and combustion of toxics and precursor of toxic, containing heteroatoms such as phosphorus, nitrogen and halogen atoms.
- Theoretical determination of thermochemical properties ($\Delta_f H^\circ_{298K}$, S°_{298K} , $C_p^\circ(T)$)
- Theoretical determination of reaction pathways and of their rate constant by means of *ab initio* rate theories using GAUSSIAN software.
- Using the CHEMKIN software, we performed simulations with the developed kinetic mechanisms. These calculations allow to analyze the main reaction pathways and the products.

References

- Glaude, P.A., Melius, C., Pitz, W.J., Westbrook, C.K., 2002. Detailed chemical kinetic reaction mechanisms for incineration of organophosphorus and fluoro-organophosphorus compounds. Proceedings of the Combustion Institute 29, 2469–2476.

2015



Combustion study of organic compounds by coupling a jet-stirred reactor (JSR) to a spectroscopic method: cw-CRDS

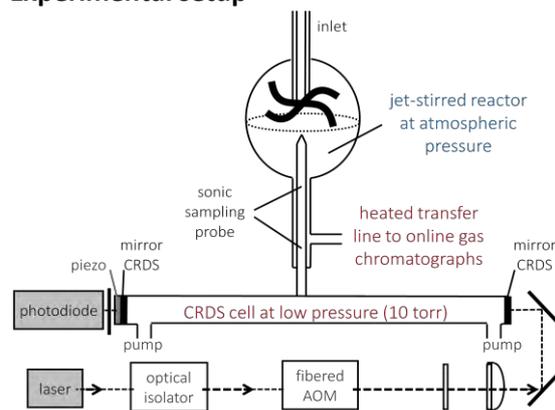
RODRIGUEZ, Anne (2013)

Battin-Leclerc F., Herbinet O.
KinCom (axe 4)

General context, scientific issues

Due to the current issue concerning the growing primary energy demand, not to mention a general interest in sustainable development, biofuels became very fashionable in recent years. They are subject to a lot of research on combustion with the characterization of the reactivity and pollutant emissions.

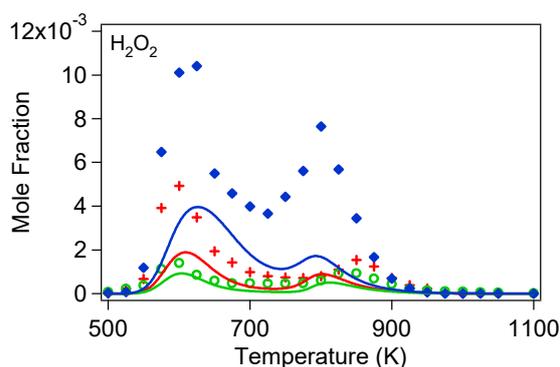
Experimental setup



Objectives and stakes

- Establish an experimental database to identify reaction products and intermediates
- Develop and validate detailed kinetic models in order to reproduce the combustion of these biofuels

Main results



Mole fractions of H₂O₂ during dimethyl-ether oxidation ($x_{\text{fuel}} = 0.02$, $P = 106.7$ kPa, $\tau = 2$ s, $\phi = 0.25, 1 \& 2$).

Symbols represent experiments and lines represent simulations with a mechanism developed in Nancy.

Methodology/ Experimental approach

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.

The products obtained have been analyzed using two complementary methods: gas chromatography (GC) and cavity ring-down spectroscopy (CRDS). The GC method is efficient in separating compounds (including isomers) and allows us to analyze a wide range of products while the CRDS method is an absorption spectroscopic technique that allows us to analyze species such as HCHO, H₂O and H₂O₂. H₂O₂ is an important reaction intermediate in combustion. Due to its fragility, it's undetectable using GC.

References

- Battin-Leclerc, Frédérique, et al. "Products from the Oxidation of Linear Isomers of Hexene." *The Journal of Physical Chemistry A* 118.4 (2014): 673-683.
- Rodriguez, Anne, et al. "Experimental and Modeling Investigation of the Low-Temperature Oxidation of Dimethylether." *The Journal of Physical Chemistry A* (2015).

2015



Study of environmentally friendly working mixtures containing ionic liquids for absorption heat transformers

El Shaimaa Abumandour (3rd year)

Fabrice Mutelet, Dominique Alonso
LRGP ThermE



General context, scientific issues

In recent years, industrial and domestic activities increased oil and fossil fuel demand while fossil fuel supplies of the world are limited and the fuel reserves are getting depleted. Moreover, environmental problems represented by the greenhouse effect and increasing CO₂ emissions have been rapidly thrust upon us. Reusing thermal waste heat streams from industrial activities, such as power stations, instead of discharging them as thermal pollutant to air and water, receives considerable attention [1]. One of the most promising devices for energy savings, which consume negligible amounts of primary energy, is the absorption heat transformer (AHT)

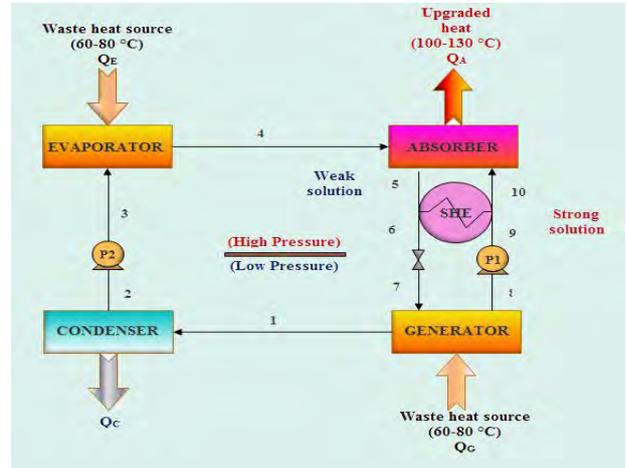
Objectives and stakes

AHT can use low temperature level heat (waste heat) to produce useful thermal energy at higher temperature level to be recycled in industrial applications. The commonly used working fluids in AHT have technical problems such as corrosion and crystallization. Our objective is to study new binary systems consisting of {H₂O + ILs} and to evaluate their performance as working mixtures in a single stage AHT cycle.

Methodology/ Experimental approach

Thermodynamic and physical properties such as vapor liquid equilibrium, heat capacity, excess enthalpy and density of binary systems composed of {H₂O + ILs} were determined in order to evaluate the coefficient of performance of these working fluids in absorption heat transformer. The vapor-liquid equilibria were measured using the boiling point method, the heat capacity and the excess enthalpy using the calorimetry (C80 or DSC III). All experimental data were correlated using thermodynamic models such as NRTL model. Simulation results on these working fluids are then compared to the already used working fluid {H₂O + LiBr}.

Illustration: Single stage absorption heat transformers.



Main results

In this work, 17 binary systems {H₂O + ILs} were studied as alternative working systems for the AHT cycle. The VLE of the binary systems showed strong negative deviation from the Raoult's law, which shows the potential of the system to be used as alternative working pair. The low values of heat capacities of the binary systems (which is beneficial to heat transfer) lead to a reduction of energy consumption and an improvement of the coefficient of performance.

While viscosity of pure ILs are high, it would decrease sharply when the ILs are heated or mixed with water.

The performance of a single-effect AHT was evaluated based on the thermodynamic properties measured, mass and energy balance of each component of the system. The simulation results show that the cycle performance of the new binary systems is close to that of already used working pair. However, the advantages of negligible vapor pressure, extended operating temperature range, no crystallization and less corrosion tendency to iron-steel material may classify the new working binary systems as the more appropriate for the industrial AHT.

References

- [1] X. Zhang and D. Hu, Applied Thermal Engineering, 2012, p 129-135
- [2] D. Alonso et al., Applied Energy, 2002, p 583-597

2015



Extraction of volatile organic compounds from aqueous mixture using ionic liquids

Amel AYAD (2nd year)

Fabrice MUTELET, Amina NEGADI



General context, scientific issues

Due to the high volatility and the significant toxicity of traditional solvents used in industry, it is necessary to find solutions to maintain a satisfactory rate of production while respecting the environment.

Growing interest is currently focused on ionic liquids (ILs). ILs are polar compounds composed of ions which are liquids below 100 °C. They have many favourable characteristics such as negligible vapor pressure, good thermal stability. Moreover, they are liquid in a large range of temperature and they can dissolve numerous organic and inorganic substances [1].

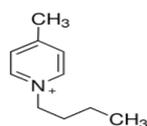
Objectives and stakes

This work constitutes a contribution to the experimental study and representation of thermodynamic properties of a new class of ionic liquids tricyanomethanide based ILs in the presence of organic compounds. The main objective is to determine their field of applications in process engineering.

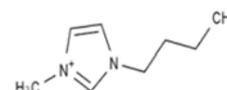
Methodology/ Experimental approach

Gas-liquid chromatography method is used to determine the activity coefficients at infinite dilution of organic solutes (alkanes, alkynes, cycloalkanes, alcohols, aromatics and ketones) in the ionic liquids. These data give also information concerning the interactions between ILs and solutes. The vapor-liquid equilibria (VLE) have been measured using a static method in a range of temperature from 283.15 to 313.15 K. The molar heat capacity has been obtained using a micro DCS III (Setaram). Densities of ionic liquids and their mixtures with water as a function of temperature were measured using an Anton Paar densimeter (Graz, Austria).

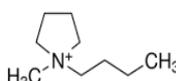
Illustration: Chemical structures of ILs investigated for measurement of thermodynamic properties



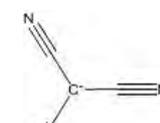
1-butyl-4-methylpyridinium



1-butyl-3-methylimidazolium



1-butyl-1-methylpyrrolidinium



tricyanomethanide

Main results

The infinite dilution activity coefficients ($\gamma_{1,2}^{\infty}$) and gas-to-liquid partition coefficients (K_L) of various solutes for the given IL were calculated from the measured retention data. Retention data were also used to estimate the capacity and the selectivity at infinite dilution of several ionic liquids for various separation problems. The results indicate that this family of ionic liquids can extract sulfur, nitrogen or oxygen compounds from a mixture.

Vapor pressures, heat capacities and densities of binary systems composed of {H₂O + 1-butyl-3-methylimidazolium tricyanomethanide} and {H₂O + 1-butyl-4-methylpyridinium tricyanomethanide} and {H₂O + 1-butyl-1-methylpyrrolidinium tricyanomethanide} were measured to evaluate the influence of the cation of the ionic liquid on the thermodynamic properties. The first results indicate that the cation has a low influence on physico-chemical properties compared to the anion.

References

- [1] J.P. Hallet, T. Welton, Chem. Rev. 111, (2011) 3508–3576.

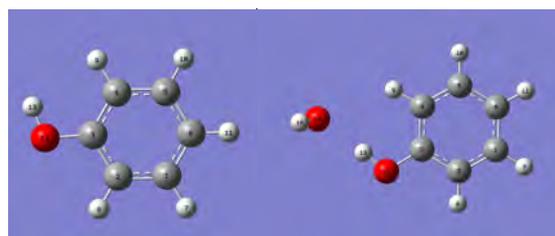
<p>2015</p> 	<p style="text-align: center;"><u>Thesis subject</u></p> <p style="text-align: center;">Cesari Laëtitia (1st Year of PhD)</p> <p style="text-align: center;">Fabrice Mutelet, Laetitia Canabady-Rochelle ThermE (axis 4)</p>	
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General context, scientific issues

Lignin is one of the major components of biomass and is a potential source of renewable aromatic chemicals. Some valuable compounds, such as phenol, guaiacol and syringol could be produced from lignin⁽¹⁾, but extraction and purification are still a huge issue.^(2,3) Moreover, few data about the physical properties of these valuable compounds are available in the literature.

Illustration

Optimized structures of phenol alone and in presence of water.



Objectives and stakes

The objective of the thesis is to extract valuable compounds from bio-oil. With a better understanding of the behavior of phenolic compounds with green solvents, it would be possible to improve extraction depending to the bio-activity of the

Main results

- Optimization of the structure of the phenol molecule alone shows that the planar conformer has a greater stability than the nonplanar one.
- The highest interaction energy between water and phenol is found when water adopts a perpendicular orientation to the plane of phenol, next to its hydroxyl group, showing a hydrogen bonding.
- Molecular dynamic simulations also highlight the presence of hydrogen bonding.
- Solubility of the phenolic compounds in water has been determined. Solubility increases with temperature for all compounds. Pyrocatechol and phenol have the highest solubility. Results are in good agreement with the literature. Further studies can be performed to model the solubility using thermodynamic approach.

Methodology/ Experimental approach

This work uses computational study and experiments. The focus is made on 8 phenolic compounds: phenol, syringol, pyrocatechol, guaiacol, o-, m-, p- cresol and vanillin. Their behaviour and proprieties will be studied in water or ethanol.

The effects of intermolecular hydrogen bonding on the molecular structure of the model compounds are studied by *ab initio* calculation with the HF, DFT and MP2 models and at different levels of theory (from 3-21 to cc-pVTZ) using the Gaussian software.

Molecular structures are also provided by *ab initio* calculations, as a stat-up for molecular dynamics. Simulations are made on the Tinker software with the OPLSAA force field.

Solubilities of the compounds are studied in a large range of temperature, by the shake-flask method and analyzed by spectroscopy

References

- [1] C. Amen-Chen, H. Pakedl, C. Roy, *Bioresource Technology*, 79, 277 (2001).
- [2] C. Amen-Chen, H. Pakedl, C. Roy, *Biomass and Bioenergy*, 13, 25 (1997).
- [3] J.N. Murwanashyaka, H. Pakdel, C. Roy, *Separation/Purification Technology*, 24, 155 (2001).

2015



Heat transfer study in an innovative evapo-condenser for seawater desalination.

Gonda, Armel (2013-2015)

Alonso, Dominique
Reactions and Reactors (ThermE)

General context, scientific issues

SOLMED (SOLar Multi-Effect Desalination) project involves the development of an innovative technology for multiple-effect distillation (MED) for sea water desalination. The project aims at sea water desalination on vertical polymer tubes using thermal solar energy, or low grade thermal waste. A five effects prototype was built in Grenoble to bring a proof of concept at a significant scale [1]: fresh water production of about 10 m³/d.

Objectives and stakes

To design and size an industrial system, it is necessary to have heat transfer models representing as accurately as possible the specificity of the technology used:

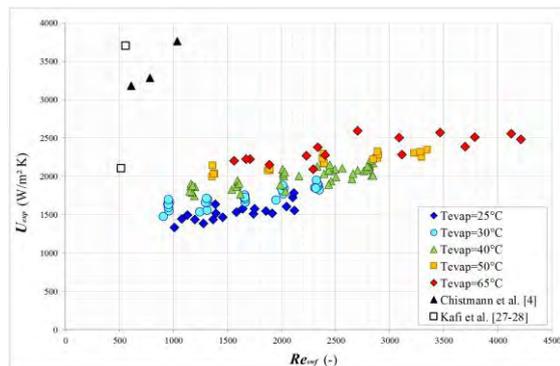
- The work consisted in developing a test rig for measuring heat transfer coefficients and the influence of operating parameters.
- Secondly, a suitable model was proposed. Its parameters were determined from experiments.

Methodology / Experimental approach

A test rig with a single polyolefin tube (50-70 μm thick, 32 mm diameter and 1.75 m of length) was built [2].

- Hydrodynamic tests and contact angle measurements were performed to study salt water film wetting on the tube surface.
- Thermal tests were carried out in order to calculate overall heat transfer coefficients.
- To reach each contribution (falling film evaporation and dropwise condensation) two new models were developed from the experimental data and appropriated correlations. According to a least square method, a numerical optimization was used to determine the parameters.

Illustration (result, methodology or context)



Main results

- Salt water flow on the outer surface of the tube improves the film wetting over time. This results in a decrease of the contact angle value of approximately 22 %. Thanks to this phenomenon, tube surface area has been entirely wetted.
- Overall heat transfer coefficients were evaluated and compared with two other studies. The achieved experimental values ranged (1300-2600 W/m² K) correspond to those expected.
- A good agreement has been observed between experimental data and theoretical prediction with an error within ± 15 %.

References

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- [2] A. Gonda, D. Alonso, V. Renaudin, T. Roques-Carmes, P. Bandelier. SOLMED: heat transfer characterisation. *In Conference on Desalination for Clean Water and Energy, Euromed 2015, Palermo, Italy, May 10-14, 2015.*

2015



Development of cubic equations of state adapted to the representation of blends made of polar molecules (water, alcohol, amines...) and hydrocarbons

Le Guennec, Yohann (1st year)

Jaubert, Jean-Noël – Privat, Romain



General context, scientific issues

The aim of this thesis is to propose new cubic equations of state able to reproduce and predict the phase behavior of mixtures made up of non-polar (hydrocarbons) and polar molecules. Mixing rules will be deduced from the incorporation of activity coefficients models in the equation of state.

Objectives and stakes

- Develop optimal α -function analytical expressions for various equations of state. Accurate predictions of properties in the super-critical domain are ensured with the use of constraints based on the expected physical behavior of the pure components in this region.
- Derive optimal mixing rules for cubic equations of state
 - A liquid phase activity model will be considered
 - A novel coupling between the activity model and the equation of state will be done
- The equation of state will be made predictive and tested on a large number of experimental data from the literature

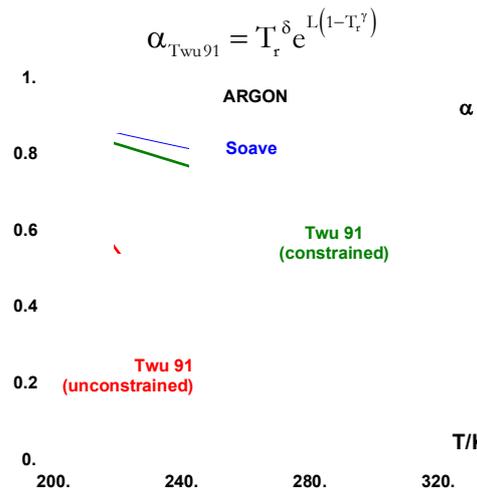
Methodology/ Experimental approach

Experimental and pseudo experimental data are taken from DIPPR, REFPROP, DDB and internal databases as well.

Reference

Twu, Chong H et al. « A Cubic Equation of State with a New Alpha Function and a New Mixing Rule ». Fluid Phase Equilibria 69

Illustration (result, methodology or context)



Predictive capacities of two α functions (Soave and Twu 91) for pure Argon

- Regressed data : P^{sat} , $\Delta_{\text{vap}}H$ and $c_{p,\text{liq}}^s$
- If the convexity of the Twu 91 α function is constrained when fitting parameters L , δ and γ , a trend similar to Soave's α function is achieved. Accuracies of the predicted properties are similar for both α functions.

Main results

- Non-volumetric properties are well predicted after re-parameterization of the Twu 91 α function
- Volumetric properties are not properly predicted and the influence of a volume translation of the equation of state has to be studied.
- Once pure compounds are well represented, focus will be put on the incorporation of new mixing rules in cubic equations of state

2015



Predicting binary-interaction parameters of cubic equations of state for petroleum fluids containing pseudo-components

Xiaochun Xu

Jean-Noël Jaubert, Romain Privat
ThermE



General context, scientific issues

Cubic equations of state (EoS) are widely used for modeling thermodynamic properties of petroleum fluids involving both well-defined and pseudo-components (P-C). However, the binary-interaction parameters (BIP) k_{ij} of a pair involving a pseudo-component are either set to zero or estimated by a specific correlation. The PPR78 and PR2SRK methods make possible the estimation of k_{ij} parameters for any cubic EoS from the mere knowledge of $\{T_c, P_c, \omega\}$ and chemical structures of components. Therefore, to calculate k_{ij} (where i and/or j are/is a pseudo-component) from the PPR78 or PR2SRK methods, the chemical structure of the pseudo-component is required.

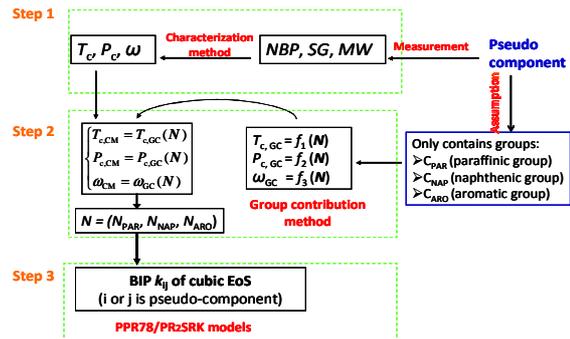
Objectives and stakes

The objective of our work is to propose an approach to predict the BIP between a pseudo-component and a real component or another pseudo-component with the PPR78 (or PR2SRK) methods.

Methodology/ Experimental approach

Our approach for predicting BIP of pseudo-component is divided into three steps. First, a so-called characterization method (CM) is employed to estimate $\{T_c, P_c, \omega\}$ of the considered pseudo-component. Secondly, it is assumed that each P-C was made up of only three groups: paraffinic group (C_{PAR}), naphthenic group (C_{NAP}) and aromatic group (C_{ARO}). Then occurrences of three groups in a P-C are determined from the knowledge of $\{T_c, P_c, \omega\}$ by using specially developed group contribution methods. Third, PPR78/ PR2SRK models are employed for estimating BIP of P-C.

Illustration: our proposed approach for predicting BIP of pseudo-component.



Main results

A solution is proposed to estimate k_{ij} (where i or j is a pseudo-component) of cubic EoS for petroleum fluids.

The group contribution methods are specially developed for estimating $\{T_c, P_c, \omega\}$ of hydrocarbons, when only considering three elementary groups: C_{PAR} , C_{NAP} and C_{ARO} .

To verify the feasibility of the present approach, the (P, T) phase envelopes of three petroleum fluids are predicted following the proposed approach and compared to those obtained by considering a very detailed structure of each pseudo component. The results are extremely close which validates the present approach.

References

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- [3] Twu et al., *Fluid Phase Equilib.* 1984, 16, 137-150

2015



Supercritical CO₂ Brayton Cycle, conception and optimization of an innovative coal-fired power plant

Qiao ZHAO (1st year)

Jean Noël Jaubert, Romain Privat, Mounir Mecheri
LRGP-EDF



General context, scientific issues

Today, world energy consumption is increasing continuously and the coal demand will reach 9 billion tonnes per year by 2019 [1]. The public awareness of thermal pollution and emission of greenhouse gases is rising yet coal-fired plant is still a key source of energy. Two main technical means intending to solve the issue are being widely studied in coal-fired plants: carbon capture and storage (CCS) and/or improvement of energy efficiency with given power output in thermodynamic power cycle.

Objectives and stakes

This study focus on the enhancement of a coal-fired plant with supercritical CO₂ (S-CO₂) Brayton cycle as power cycle. The main purpose of this project is to propose an optimal/improved design of such cycle as well as such plant. Indeed, a 10%-LHV efficiency improvement is announced compared to a traditional water stream Rankine cycle in coal-fired plant [2]. The idea of optimization incorporates the design and operating parameters. Moreover, the key components (turbine, compressor and boiler) are to be analysed and detailed with 1.5 dimension design.

Methodology/ Experimental approach

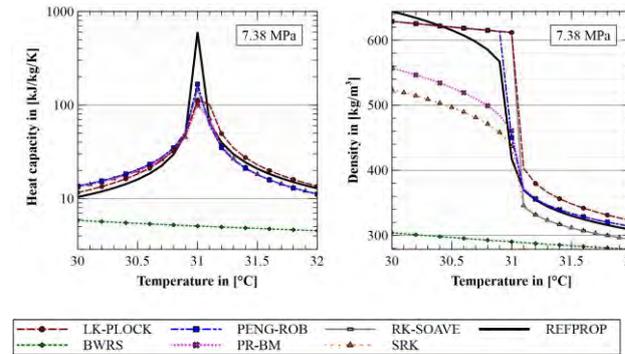
For the validation step, a process simulator ProSimPlus version 3 is chosen in order to evaluate different thermodynamic models. Since fluid properties have strong influences on turbo-machinery, it is important to have a model which is capable of well predicting performances of supercritical fluid.

Then a calibration is to be done with steam cycle in order to test the limits of the software.

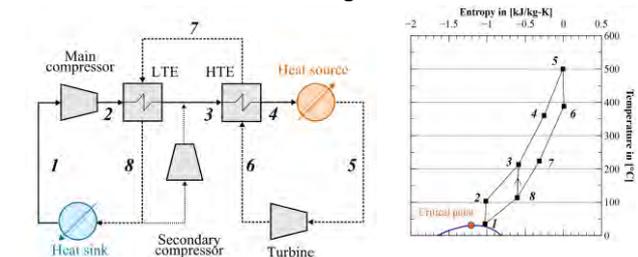
Moreover, modeling, simulation and optimization of entire S-CO₂ Brayton power cycle will be carried out through this software.

Illustration:

(a) Thermal capacity isobaric and density around the critical point of CO₂



(b) Single recompression CO₂ closed Brayton cycle and its T-S diagram



Main results

The current bibliography research shows that the S-CO₂ Brayton cycle has been widely investigated in nuclear reactor and solar thermal plant applications. Results indicate that conception of this cycle could improve energy efficiency and that a more compact turbo-machinery can be achieved.

Future works aim to (i) verify Span&Wagner equation with DECHEMA data around critical zone of CO₂; (ii) study on the calibration of Rankine steam cycle and optimize through process simulator and finally (iii) carry out modelling and techno-economic optimization of S-CO₂ process.

References

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Processes For Products And Materials



LABORATOIRE
REACTIONS AND



REACTIONS ET GENIE DES PROCEDES
CHEMICAL ENGINEERING LABORATORY

2015



ZnO nanoparticles for bacterial inactivation by photocatalysis.

Faouzi ACHOURI

Raphaël Schneider / Serge Corbel

PROCESSES, PRODUCTS AND MATERIALS

(Elaboration and formation of dispersed materials)



General context

Environmental disinfection plays a crucial role in the prevention of infectious disease. In recent years, environmental and opportunistic bacteria have been responsible for a large number of disease outbreaks in a variety of settings. Moreover, the increase in microorganism resistance to commonly applied chemotherapeutics and disinfectants constrain the development of new agents for disinfection.

Materials like ZnO and TiO₂ are important photocatalysts that provide a relatively simple means for the conversion of solar energy for use in oxidation and reduction processes. Photocatalysis is applied in many areas including the elimination of contaminants from water and air, odor control, water splitting to produce H₂, inactivation of cancer cells, and many others[1, 2].

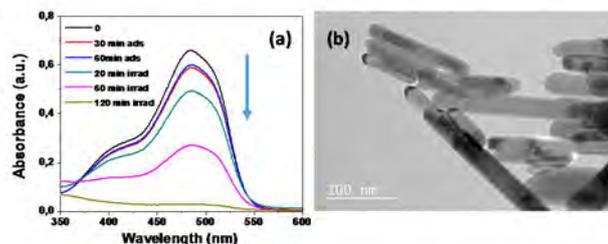
The aim of our work is the evaluation of the photo-activated antibacterial activity of ZnO-based nanomaterials.

Objectives and stakes

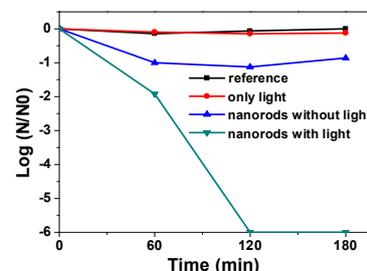
Synthesis and characterization of ZnO nanoparticles (spheres, rods,...). Evaluation of the morphology on the photocatalytic activity. Doping of ZnO nanoparticles to increase the visible light activity of photocatalysts for bacteria inactivation.

Methodology/ Experimental approach

- Development of new solvothermal and hydrothermal methods to produce ZnO or doped-ZnO nanoparticles with controlled morphology. Characterization of the materials by SEM, TEM, XRD, UV-visible spectroscopy,...
- Evaluation of the photocatalytic activity of the new materials using the orange II dye as a model pollutant.
- Application to the elimination of the microorganisms like bacteria in waste water.



(a) Degradation of orange II using ZnO nanorods under visible light, (b) TEM micrographs of ZnO nanorods.



Inactivation kinetics of *E. coli* MG 1655 with ZnO nanorods under solar light.

Main results

- ZnO nanorods undoped and doped with Mn²⁺ have been successfully synthesized.
- ZnO nanorods doped with Mn prepared via hydrothermal methods generate more ROS ([•]OH and O₂⁻radicals) than ZnO particles and their photocatalytic activity is enhanced.
- Inactivation of bacteria *E. coli* bacteria is highly efficient using ZnO nanorods.

References

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- [2] P.K. Dutta, S.O. Pehkonen, V.K. Sharma, A.K. Ray, Photocatalytic oxidation of Arsenic (III): evidence of hydroxyl radicals, Environ. Sci. Technol. 39 (2005) 1827–1834.

2015



Calcium carbonate precipitation under very low supersaturation level:

Study of mineral fouling

Lubin Chauvot de Beauchêne (3rd year)

Hervé Muhr
EMMAD



General context, scientific issues

Fouling is the deposition of substances on the walls of pipes and other structure conveying water. It causes the pressure drop as well as the thermic resistance to increase and can cause blocking, heavily impacting any process concerned.

Tap water distribution is done through underground coated pipes, which are installed for decades making them subject to mineral and biological fouling. The consequences are the cleaning or replacement of the impacted sections. These operations boast heavy costs and are to be reduced as much as possible.

Objectives and stakes

A work group has been created to study different polymer coatings for pipes to select the one best suited in regard to decreasing the mineral and biological fouling. We focus on the former. This work is also the opportunity to study CaCO_3 formation at low supersaturation level (CaCO_3 being the main component of mineral fouling) and the influence of the surface of deposition on the mechanisms involved.

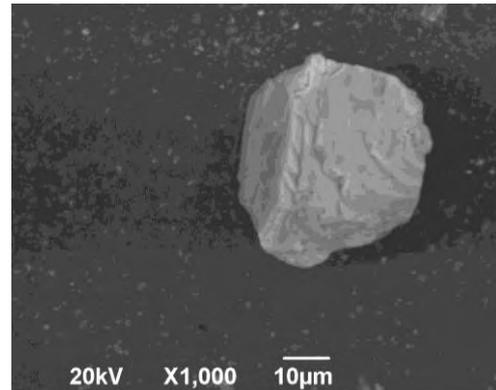
Methodology/ Experimental approach

The first part of the thesis was the creation of a pilot process for the deposition of CaCO_3 under low supersaturation using tap water. This meant using mild enrichment techniques, excluding heavy chemical influence or physical treatment of the medium. Once the pilot was created, a methodology has been formulated to test the materials provided:

The materials are tested for 72h as batches of five samples in the presence of reference samples. Those samples of deposits are observed (MEB) and then dissolved and dosed through ICP-OES. A quick conversion gives the amount of mineral by area unit. The data are then statistically compared across the studied and reference materials.

Illustration:

Calcite crystal forms after 72h on a reference material



Main results

The first result is the assembly of an entirely new process of low supersaturation deposition of CaCO_3 able to work under 83mg/l.

The methodology developed for the testing and analysis of the material samples allows for the accurate measure of the mineral formed on its surface.

The kinetic study of deposition showed a steady increase in deposit, excluding a surface formation and growth mechanism alone and pointing to a combined deposition and growth mechanism.

The observation of the crystals showed calcite, the most stable form of calcium carbonate, as expected.

The statistical comparison of the deposits showed little difference for the first generation of materials, yet we were able to orient the choice for later generation, until the third generation of materials which showed statistically lower deposits than the reference.

References

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2015



Photocatalytic microchannel reactors using metal-oxide semiconductors sensitized with CuInS₂ quantum dots

DONAT Florian

Raphaël SCHNEIDER / Serge CORBEL / Didier ROBERT
 PROCESSES, PRODUCTS AND MATERIALS
 (Elaboration and formation of dispersed materials)



General context

Medicinal drugs constitute a new type of pollution in hospital effluents. Ifosfamide, one of these drugs is a highly toxic anticancer agent due to its mutagenic, carcinogenic and teratogenic properties.

Photocatalytic^[1] degradation has been investigated over the last years to solve environmental problems and to degrade pollutants in waste water. TiO₂^[2], one of the most used semiconductor photocatalyst, has a modest efficiency due to the fast recombination of photo-induced charge carriers. Moreover, TiO₂ can only be activated under UV light.

Quantum dots (QDs) like CuInS₂^[3] can be coupled with TiO₂ to increase the efficiency of photo-catalytic processes (charge separation increase) and make this photocatalyst highly efficient under visible light irradiation

Objectives and stakes

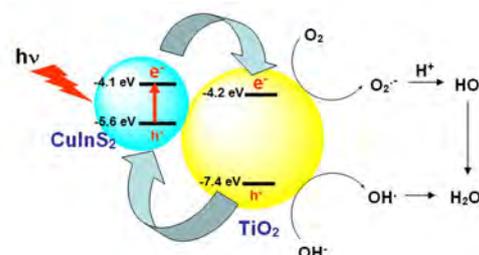
- Development of efficient solar and/or visible light active photocatalysts.
- Evaluation of their ability to photodegrade Ifosfamide in batch reactors and in tubular microreactors.

Methodology/ Experimental approach

Core/shell CuInS₂/ZnS QDs were prepared by high temperature decomposition of organometallic precursors. These dots were next associated to TiO₂ at high temperature to create a heterojunction between the two semiconductors. Various synthesis parameters have been evaluated like (i) Cu : In ratio, (ii) TiO₂ : QDs ratio, or (iii) the calcination temperature.

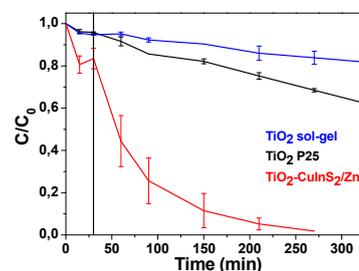
The Orange II dye degradation was monitored by UV/vis spectroscopy, and Ifosfamide via HPLC.

Illustration of photocatalysis



Under visible irradiation, electrons of CuInS₂ QDs are excited from the valence band (VB) to the conduction band (CB). The electron photo-generated in CuInS₂ CB moves to TiO₂ CB while an electron of TiO₂ VB moves to CuInS₂.

Main results



- Using Orange II as model pollutant, the TiO₂-CuInS₂ photocatalyst is highly active under visible light or under solar light irradiation. Experiments with Ifosfamide are in progress.

References

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2015



Textile functionalization by dry powders impregnation for flame retardance properties

Karine Gerardin (3rd year)

Véronique Falk, Laurent Perrin, Olivier Dufaud
PROCESSES, PRODUCTS AND MATERIALS
(Elaboration and formation of dispersed materials)



General context, scientific issues

The chemical or physical functionalization of nonwoven textile is used to provide additional performance to the initial fibre. Both new functional requirements and sustainable development drive the development of new materials with advanced properties as aesthetics and fashion, functionality and performance. Evolving in highly competitive markets as building, transport, health, sport, etc..., European textile companies need to innovate, differentiate to remain. In construction, transport and furniture sectors, flame-retardant products are needed which implies to treat synthetic textiles and foams to reach this end-use property. Develop a greener way is a challenge to take up.

Objectives and stakes

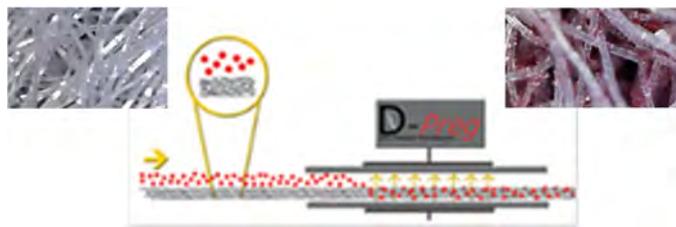
FOMOTEX project is a FUI project (BPI France). Technical and industrial objectives are to develop coatings without latex for nonwoven textiles or technical foams having multipurpose characteristics and in particular flame retardance (FR) properties which answer the safety standards and are in agreement with a sustainable development strategy.

Methodology/ Experimental approach

The methodology of this experimental work is based on inverse product design methodology. First, end-use properties were identified using products standards. The chosen process, D-Preg, allows of only dry powders which avoids the use of solvents. Then, the work has been focused on the development of powders blends which associate binders and flame retardants. Various materials and mixing processes have to be studied. Moreover, the use of high voltage electric fields as well as flammable powders requires also the consideration of the specific risks to the electrostatic technology. Finally, the target is to reach products and processes specifications, while keeping in mind the criteria of economic and industrial viability, essential point for the project success.

Illustration : DPreg impregnation Process

- A. Surface powder dusting,
- B. Particle migration due to alternating current field,
- C. Impregnation in the thickness of the porous support.



Main results

The experimental studies allow us to conclude that :

- Fireproof property is influenced by the quality of the mixture, the nature of the flame retardant agent and its availability after fixing.
- Rate and nature of components plays on rigidity and quality of the fixation of the finished product
- Presence of conductive fine particles have an unfavorable influence on the quality of the migration
- Impregnation process may lead to particle segregation what influences the final result

In order to avoid segregation in the electric field, the formulation step leads to the determination of the optimal mixture composition. A dedicated blending protocol for improving the stability of the mixture has been established. The fireproof result of M2 class, equivalent to commercial product was validated. The rigidity value of the finish product is decreased but the mixtures flow properties are improved which allows to avoid the addition of glidant and minimizes the powders flammability risks. By establishing the links between physical characteristics of components and end-use products properties, we propose a standardized method for raw materials selection for a given field of application and an optimal use of the D-Preg process. This study allowed to obtain fireproof performances without addition of solid or liquid additives. These studies must be carried on to optimize all the stages of the process and consider the transfer to an industrial scale.

2015



Study of Mechanisms Involved in the Tetravalent Uranium Oxalate Precipitation at Low Supersaturations

Alexandra Gutiérrez Chavida (3rd year)

Hervé Muhr
CEA Marcoule



General context, scientific issues

In the nuclear industry, the precipitation of the tetravalent uranium oxalate $U(C_2O_4)_2 \cdot 6H_2O$ has a specific importance in the recycling of the spent nuclear fuel as described in [1, 2]. This operation is very sensitive to several parameters, i.e. reagent concentrations, temperature, supersaturation, reactor design and mixing, controlling the quality of the precipitate.

Several studies were performed to identify the mechanisms involved during the uranium oxalate precipitation. Combining laboratory batch systems with a simple mathematical treatment of the experimental data allowed the nucleation and crystal growth rates of this salt to be determined [1]. Agglomeration kinetics and hydrodynamic effects were studied continuously in a Mixed Suspension Mixed Product Removal reactor (MSMPR) [2, 3]. All these kinetic studies were carried out under high supersaturation ratio values, i.e. up to 2000. Under low supersaturation ratio no data is available dealing with the secondary nucleation and crystal growth mechanisms.

Objectives and stakes

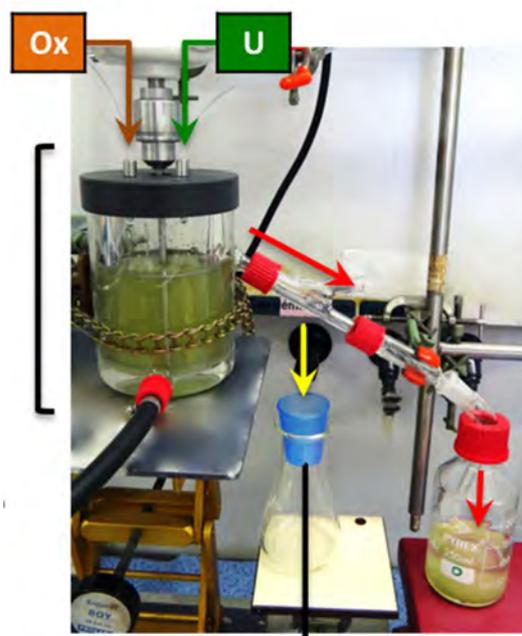
The aim of this thesis is to study the precipitation of $U(C_2O_4)_2 \cdot 6H_2O$ in a MSMPR with very low supersaturation values.

Complementary solubility tests of this oxalate are performed at different conditions. This data is required to calculate the supersaturation ratio at continuous precipitation experiments.

Methodology/ Experimental approach

The tetravalent uranium oxalate precipitation $U(C_2O_4)_2 \cdot 6H_2O$ has been performed at low supersaturation in a continuous MSMPR reactor. The device operates with a constant and homogeneous supersaturation in all its volume. The kinetic parameters can be evaluated using the population balance resolution.

Illustration: Experimental set-up in operation.



Main results

Solid and liquid phases are analyzed providing enough data to have an overview of the process. The XRD and SEM images certify the precipitation of the desired form. The ICP-AES and granulometry give the total uranium concentration and the PSD throughout the test proving that 5τ are enough to achieve a constant uranium concentration, while 7τ are necessary for the PSD to reach a steady state. Further studies will focus on the mathematical treatment in order to determine the nucleation, crystal growth and agglomeration kinetics occurring at low supersaturations. Solubility tests have provided satisfactory results. A modelling has been developed in order to calculate solubility at different acidity and oxalic excess.

References

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2015



Synthesis the nanocrystals of semiconductors using microfluidic device in aqueous medium

KOLMYKOV Oleksii

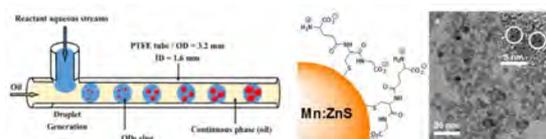
Raphaël Schneider / Jean-Marc Commenge
PROCESSES, PRODUCTS AND MATERIALS

(Elaboration and formation of dispersed materials)

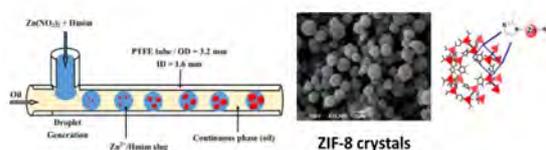


General context

Since ten years, it has been demonstrated that microreactors may offer a great variety of advantages over batch systems for the synthesis of nanoparticles. Among them, efficient mixing, precise temperature and reaction times control, allow the preparation of monodispersed nanoparticles. Moreover, microfluidic devices provide potential for automating multi-step processes (analysis, surface functionalization and purification in a single microchip) and for the preparation of large quantities of nanocrystals through a continuous process.



Schematic of the segmented flow, and HR TEM image of QDs



Schematic of the segmented flow, and SEM image of ZIF-8 nanoparticles

Objectives and stakes

- Develop new aqueous-based microfluidic continuous syntheses of highly luminescent quantum dots (QDs) using either single phase flow or two-liquid segmented-flow devices [1].
- Adapt the segmented-flow reactors to the production of metal-organic frameworks (MOFs) like zeolitic imidazolate frameworks (ZIFs) [2,3].

Main results

- Highly luminescent 3-mercaptoproponic acid (MPA)-capped Mn-doped ZnS QDs can be synthesized using a two-liquid segmented-flow microreactor.
- Large quantities and size-controlled ZIF-8 nanocrystals can be produced either via a two-step integrated microfluidic synthesis in a continuous-flow mode using a T-type micromixer.
- Flow rate, reaction time, temperature and oils influence the quality of the nanoparticles produced (size, size distribution, specific surface, and pore volume) after the microfluidic synthesis.

Methodology/ Experimental approach

Segmented flows are composed of two immiscible phases: one dispersed phase (reactant in aqueous stream) and one continuous phase (oil stream). The droplet consists of the dispersed phase and the continuous phase encapsulates the droplets and preferentially wets or coats the surface of the microchannel.

For the microfluidic system, syringe pumps were connected by means of teflon tubing to combine dispersed phase with the continuous stream. Nanoparticles produced were characterized by TEM, SEM, XRD, UV-visible and fluorescence spectroscopies,...

References

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2015



Thermohydraulic modelling of a continuous supercritical water oxidation process – incorporation of the precipitation of mineral species



Gaëtan Lemoine (1st year)

Hervé Muhr¹, Hubert-Alexandre Turc²

¹LRGP, ²CEA (DEN/DTCD/SPDE)

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.

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]. A more complete model has to be developed with the aim of predicting inorganic salts behaviour inside the autoclaves. The objective of this work is to take into account salt precipitation in the numerical model.

Methodology / Experimental approach

Some experiments will be carried out in order to study precipitation and to produce experimental data useful for the model, for example the solubility of various inorganic salts.

An experimental apparatus will be designed which consists in an autoclave of inner volume 0.6L, fed with a continuous stream with known salt concentration. Due to higher temperature and pressure in the reactor, oversaturation occurs and precipitation takes place. As a result, the concentration of the outlet stream is the solubility of the studied salt. The solubility of each salt in the range of $350\text{-}500^\circ\text{C}$ at 30 MPa (SCWO's typical operating conditions) is determined with this method.

Illustration: Batch autoclave that will be used for salts solubility measurements.



General approach and expected results

Solubility data obtained via the batch apparatus described above, but also by a high pressure calorimetric analyser, will then be implemented in a population balance equation considering nucleation and agglomeration (crystal growth can be neglected due to his low rate), which will be used in the CFD model to predict precipitation.

Beside the integration of precipitation, several other improvements are possible to enhance the precision of the numerical model. First of all, some work must be carried out concerning the choice of an equation of state able to calculate the thermodynamic properties of mixtures of water, gases and salts at a pressure of 30 MPa and on a large range of temperature. According to literature, a Volume-Translated Peng-Robinson equation might be a good compromise between accuracy and computing costs. Next, the numerical model for combustion also needs to be corrected, by some experimental measurements of kinetic parameters, and by the use of a better combustion model, for example a PDF model.

References

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2015



Modelling study on the uranium peroxide precipitation in a fluidized-bed reactor

Luz Adriana MOJICA (3rd year)

Hervé MUHR, Edouard PLASARI, Murielle BERTRAND
EMMAD. CEA Marcoule



General context, scientific issues

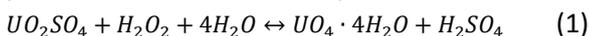
In the processing of uranium ores, the uranium is recovered from mill leach solutions by precipitation as yellow cake concentrates. The fluidized bed reactor (FBR) is widely used in industrial precipitation processes. Particularly, a continuous precipitation of uranium by hydrogen peroxide in FBR is developed by AREVA [1]. The benefit of these processes is to lead a high-quality of solid particles of uranium peroxide in terms of granulometry, morphology, purity and density, which is an advantage in filtering operations as well as downstream handling of the powder.

Objectives and stakes

The aim of the present study is to give the experimental requirements that combined with the process modelling will provide the support for the optimization and design of the process to any operating conditions of the uranium peroxide precipitation.

Experimental approach

The uranium peroxide precipitation is produced at room temperature by mixing an uranyl sulfate solution with hydrogen peroxide according to the following precipitation reaction (1). The hydrogen peroxide (35%) is added to get a hydrogen peroxide-to-uranium ratio of 1.5:1. The flow rates are adjusted so that to create a fluidization of the particles with a fluid velocity of about $2 \text{ mm}\cdot\text{s}^{-1}$.



The reaction must be performed at $\text{pH} = 3$. Due to the influence of the pH on the precipitation kinetics [2], the follow up and control of the pH is a determinant key. Thus, the pH is adjusted using a sodium hydroxide solution with a concentration of 200 g/L . A pH probe is situated at the top of the settler, allowing continuous monitoring of the pH which must be varied between 2.8 and 3.5.

Main results

The uranium peroxide solid particles obtained by precipitation in the fluidized bed reactor are compact agglomerates characterized by a relatively narrow size distribution (Fig. 1).

Figure 2 shows the variation of the mean particle size of the precipitate from the beginning of the experiments until the establishment of the stationary regime. First, during the non-stationary regime, the variation of the mean particle size is almost the same due to the initial solid charge used to start-up the experiments. Further, after the discharge of the initial solid charge, the stationary regime is gradually established showing the real mean particle size which can be obtained in the fluidized bed reactor under prefixed operational conditions. Here, it is very interesting to note that when the rotating speed is increased two times (Experiment 2), the mean particle size sharply decreases. This cannot be explained by the phenomena of attrition or breakage of the agglomerates [3].

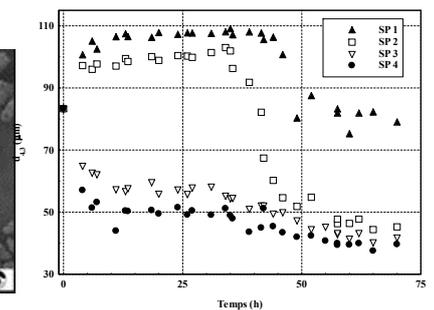
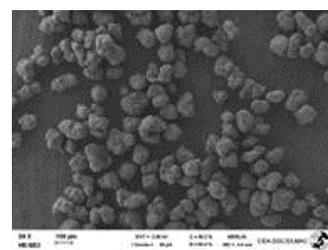


Figure 1 (gauche) - Figure 2 (droite) : SEM photos of the uranium peroxide formed in the FBR - Variation of the mean particle size with time for the Experiments 1, 2 and 3 at the bottom of the reactor

References

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2015



ZnO Quantum Dots Doped with Cu: Structural, Morphological, Optical and Bacterial Studies

Hatem Moussa

Raphaël Schneider and Ben attia Mossadok
PROCESSES, PRODUCTS AND MATERIALS

(Elaboration and formation of dispersed materials)



General context

ZnO particles are generally considered to be of very low toxicity and biosafe. However, when reduced to the nanoscale, ZnO shows new aspects of toxicity [1]. The ecological response to ZnO nanoparticles (NPs) has only weakly been investigated despite the fact that their release into the environment is inevitable due to their high level of production. Several reports pointed out that ZnO NPs generate oxidative stress through the production of reactive oxygen species (ROS) like hydroxyl radicals ($\cdot\text{OH}$) and superoxide radical anions ($\text{O}_2^{\cdot-}$) and that these species may dominantly contribute to the antimicrobial activity of ZnO NPs [2].

With this respect, it is worth mentioning that most toxicity studies on ROS generation from ZnO NPs were conducted in deionized water. However, natural waters always contain cations which may complicate the behavior of ZnO NPs and their toxicity. Cu^{2+} is an important representative of cations present in the natural environment and the consequences on toxicity of its interaction/association with ZnO nanoparticles have never been evaluated.

Objectives and stakes

We wish to assess the risks and problems associated with ZnO NPs in terms of toxicity and stability. The main objective of this research was to study the influence of Cu^{2+} association on the toxicity of ZnO quantum dots (QDs).

Methodology/ Experimental approach

The work is divided into 3 parts:

- Synthesis and characterization (UV-visible and fluorescence spectroscopies, TEM, XRD, DLS,...) of ZnO QDs either doped with Cu^{2+} ions in the crystal lattice or Cu^{2+} ions chemisorbed at their surface.
- Evaluation of ROS photo-production.
- Bacterial toxicity of the various particles.



Fig. 1. Schematic representation of the ZnO-based QDs used in this study. (a) ZnO@APTMS, (b) ZnO:Cu@APTMS, and (c) ZnO@APTMS/Cu.

Main results

- The results in this work demonstrate that the photo-induced production of ROS ($\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and H_2O_2) is markedly increased with ZnO@APTMS/Cu QDs probably via the interaction of photo-excited electrons and holes in ZnO QDs with O_2 and H_2O combined with Cu^{2+} -mediated Fenton reactions [3].
- Cytotoxicity experiments carried out on *E. coli* cells showed that ZnO@APTMS/Cu QDs were more toxic than the two other QDs and clearly pointed out the importance of the presence of Cu^{2+} ions at the periphery of the nanocrystals.
- Our study demonstrates that both the production of ROS from ZnO QDs and their toxicity may be enhanced by chemisorbed Cu^{2+} ions, which could be useful for medical or photocatalytic applications.

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Studies on the chemical behavior of sodium fire aerosols during atmospheric dispersion

Alice Plantamp (3rd year)

Hervé Muhr¹, Thierry Gilardi²

¹ LRGP - EMMAD – ² CEA, DEN - Cadarache



General context, scientific issues

The use of liquid sodium in Sodium cooled Fast Reactors (SFR) circuits, requires to study the consequences of a sodium fire, and particularly the toxicological impact of sodium fire aerosols, which can be potentially released in the atmosphere. In contact with air, liquid sodium can ignite a fire. These sodium aerosols are composed of a combination of NaOH, Na₂CO₃ and NaHCO₃. A reduction of the acute toxicity thresholds characteristics of these aerosols has recently been applied. This imposes a less conservative approach than that used in the past and based on a more accurate assessment of the evolution of aerosols' chemical composition.

Objectives and stakes

A preliminary kinetic model based on the shrinking core description was developed to calculate the chemical conversion of soda aerosols into sodium carbonate (limiting step). This model was validated with experiments for small particles (diameter around one micron) and relative humidity higher than 20% [1]. But, this model needs to be improved and to be validated with more accurate experimental data.

Methodology/ Experimental approach

Studies by Colle [2] reveal that the reactive absorption of CO₂ in a sodium hydroxide solution can be used to describe carbonation kinetic reactions. After integrating this mass transfer resistance, the model is compared to the available experimental results in the literature and the new ones coming from an experimental device. This device was developed to study the physicochemical behavior of aerosols generated from a sodium fire in controlled conditions of atmosphere composition (especially water vapor content) and for an appropriate sampling of aerosol (conditioning under inert gas). A part of this device is designed to sample at given times the aerosols by filtration, for chemical speciation.

Illustration: Experimental device designed for monitoring the physicochemical behaviour of aerosols from a sodium fire



Main results

A reactive absorption model based on the two-film theory is adapted to describe the chemical behaviour of aerosols produced by sodium fires during their atmospheric dispersion. The first comparisons carried out using data of the literature (including the latest from [3]) seems enough satisfactory to validate this model. These preliminary comparisons must however be confirmed by new experimental data covering a broader range of relative humidity and better controlled atmospheric conditions.

Four successful experiments are carried out at relative humidity of 20% (around 75°C) and of 40% (around 60°C), and at CO₂ concentration of 390 ppm, which are in good agreement with the model. The further experiments will be performed in order to show the influence of relative humidity (up to 80%) on the chemical conversion of NaOH aerosols, in order to validate the reactive absorption model for a large range of relative humidity. Then this model will be implanted in the atmospheric dispersion code used for the toxicological impact studies.

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2015



Hybrid nanomaterials: synthesis, characterization and processing

Aleksandra SCHEJN (3rd year of PhD)
 Raphaël SCHNEIDER, Véronique FALK
 PROCESSES, PRODUCTS AND MATERIALS
 (Elaboration and formation of dispersed materials)



General context, scientific issues

Metal organic frameworks (MOFs) are porous crystalline materials composed of metal ions or clusters of metal ions coordinated with organic linkers. MOFs exhibit tunable structures, low density, ultrahigh surface area and have potential applications in heterogeneous catalysis, hydrogen storage, and adsorption/separation of liquid or gaseous mixtures. Among the MOFs structures, the zeolitic imidazolate frameworks (ZIFs) have recently attracted considerable attention. In these materials, metal atoms such as Zn^{2+} are linked through N atoms by the ditopic 2-methylimidazolate ligand to form neutral frameworks. ZIF-8 has a sodalite zeolite-type topology with cages of 11.6 Å and pores of 3.4 Å in diameter. ZIF-8 are characterized by high thermal stability (550 °C in N_2), large surface area (BET: 1700 m^2/g) and high thermal and chemical resistance to various solvents. These endow possibility to use it widely in the catalytic reactions.

Objectives and stakes

- Preparation of ZIF-8 materials and ZIF-8 heterostructures with properties adapted to the desired application.
- Shaping of the materials for the industrial scale-up use.

Methodology/ Experimental approach

- rational design and optimization of the protocols for ZIF-8 synthesis: test of different precursors to modulate size, morphology and properties, doping of the framework with Cu^{2+} catalytically active sites, incorporation of Fe_3O_4 nanoparticles for magnetic separation and recyclability,
- characterization: TEM, SEM, XRD, TGA, BET surface area, SQUID,
- Evaluation of the catalytic properties and of new nanomaterials, recyclability and recovery of the catalysts,
- Compression of the material. Influence of tableting on properties.

Illustration



Main results

- By varying Zn^{2+} precursors used for the synthesis, we demonstrated that the properties (size, porosity,...) of ZIF-8 crystals can be controlled and tuned depending on the applications.
- ZIF-8 crystals were successfully used as heterogeneous catalysts in Knoevenagel and Friedländer reactions.
- Cu^{2+} -doped ZIF-8 crystals were for the first time used for Cu-mediated reactions, like Combes and Huisgen cycloadditions. The nanomaterials could be reused up to 10 times without loss of catalytic activity.
- ZIF-8 materials functionalized with Fe_3O_4 particles can easily be recovered by magnetic separation after catalytic experiments.
- Compressed ZIF-8 crystals (tablets) were used for the conversion of CO_2 into cyclic epoxides using a Parr reactor.

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2015



Study of the agglomeration during the synthesis of nanometric Precipitated Calcium Carbonate by carbonation

Mathilde Schnebelen (3rd year)

Hervé Muhr, Edouard Plasari
EMMAD



General context, scientific issues

Precipitated calcium carbonate (PCC) is a mineral filler for various applications in paints, paper, ink, pharmacy, cosmetics, etc. It can be industrially synthesized through several ways but the most common is the carbonation route. It consists in bubbling carbon dioxide in a suspension of lime to get particles of precipitated calcium carbonate. However, a challenge related to the synthesis and the use of this precipitate is the control of the agglomeration. Indeed, the precipitated nanoparticles are agglomerated in micrometric "loose" structures [1].

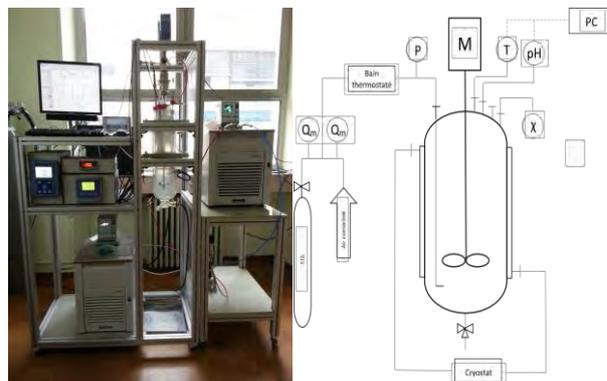
Objectives and stakes

This agglomeration has consequences on the run of the process and the properties of the final product. Thus, the aim of this work is to understand the mechanism of the agglomeration, to study its kinetics and the impact of different process parameters under complex industrial conditions characterized by a high solid concentration, intensive mechanical stirring and gas bubbling.

Methodology/ Experimental approach

To study the agglomeration, a pilot installation has been developed, which is a scale down of the industrial reactor including all the equipment and instrumentation necessary to monitor the different operating parameters of the process. Furthermore, samples are collected all along the reaction in order to follow the evolution of the PCC particle size distribution. The method to determine the agglomeration kernel β and constant β_0 is based on the resolution of a population balance using the moment approach and including terms of nucleation, growth and agglomeration [2]. Provided that the kinetic rates of nucleation and growth are known [3], the agglomeration kernel can be obtained from a mathematical treatment of the experimental particle size distributions.

Illustration: Pilot Installation



Main results

Experiments performed with a high concentration in sodium chloride (2 M) show that the modification of the electrostatic environment does not change the particle size distribution or the morphology of the agglomerates, so the electrostatic interactions are not responsible of the agglomeration. The main mechanism of agglomeration is the building of crystalline bridges between the elementary particles of calcium carbonate induced by the crystal growth.

Thus, thanks to an agglomeration kernel model including the crystal growth, it is possible to determine the value of the agglomeration constant using a mathematical treatment of the experimental particle size distributions. Finally, by varying different process parameters, it also appears that the agglomeration constant increases with temperature whereas there is an optimum for the shear rate. Regarding to this fact, we can also propose an expression of the agglomeration constant β_0 as a function of the shear rate, which can be used to control the agglomeration in the industrial reactor.

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2015



Stability of the Taylor-Couette flow of complex fluids

AGBESSI, Yao (4th year of PhD)

Lionel Choplin & Cécile Lemaitre
LRGP UMR7274 CNRS (axis 5)



General context, scientific issues

The concepts of hydrodynamic instabilities were applied to the circular Couette flow for shear-thinning fluids. When increasing the Reynolds number of a flow, it passes gradually from an ordered state, called laminar, to a chaotic state, called turbulent. During this transition, organized hydrodynamic structures appear which disorganize under successive destabilizations. These structures may cause problems for example for the homogenization of suspensions, because particles may get trapped in the structures, leading to under or over-concentrated zones. Furthermore, most of the fluids in nature and industry are non-Newtonian. In order to better understand and control the apparition of hydrodynamic structures in such fluids, we focused during this PhD on the instability mechanisms governing the transition to turbulence of complex fluids.

Objectives and stakes

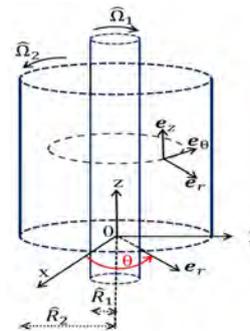
Understanding the stability and transition to turbulence for complex media in Taylor-Couette flow.

Methodology/ Experimental approach

In a theoretical and numerical approach, the destabilization of the circular Couette flow was studied to predict the apparition of structures such as Taylor vortices at long time behavior of small perturbation. An analysis at short time was also performed to study the phenomena of transient growth.

In an experimental approach, a Taylor-Couette device was designed. First, the torque on the inner cylinder was measured. Secondly, rheological measurements were conducted in order to select fluids matching models of the theoretical approach. Visualizations were then performed to detect the apparition of instabilities and critical conditions were compared to those predicted by the linear stability analysis. Finally, PIV measurements provided velocity fields in the flow.

Illustration



Main results

Theoretical and numerical approach

- For counter-rotating cylinders, the shear thinning character with or without low yield stress has destabilizing effects. On the contrary, a high yield stress produces stabilization.
- The shear-thinning character without yield stress is found to enhance considerably the optimal energy amplification of the perturbations, while the yield stress reduces it significantly
- For Newtonian fluids, the energy amplification is found to scale as $Re^{2/3}$ everywhere in the stable domain, except on the Rayleigh line where it scales as Re^2 .
- For non-Newtonian fluids, the amplification scales as $Re^{2/3}$ everywhere.
- For Re^2 scaling the anti-lift-up mechanism prevails.
- For $Re^{2/3}$ scaling, a three-dimensional Orr mechanism is at work.

Experimental approach

- Chaotic flow due to the shear-thinning character of the fluids.

References

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2015



Mass transfer within complex media. Reverse engineering: from final target property to material

AGUILERA MIGUEL, ANTONIO (1st year of PhD)

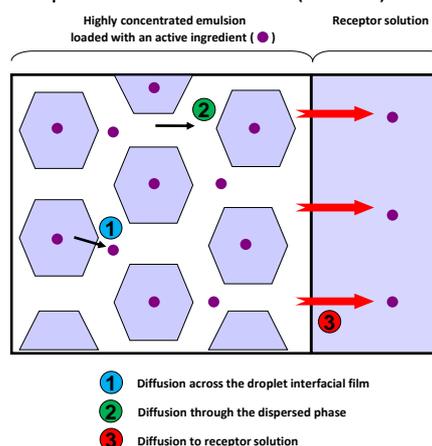
Christophe Castel (Director), Véronique Sadtler (Codirector)
LRGP-UMR CNRS 7274 (RP2E section CNU 62)



General context, scientific issues

In recent years, increased attention has been focused on novel controlled release systems within pharmaceutical, food and cosmetic industries. However, procedures to systematize the design of these complex products should also be developed. The reverse engineering technique is ideally suited to handle problems of the “define target and match target” type. With the availability of appropriate models and optimization algorithms, it is possible to develop systematic methodologies for the design of this kind of products, avoiding the common and most preferred experimental-based and trial-and-error approach, which requires a large amount of resources and a long time for product development.

Illustration: Sketch of diffusion steps from high internal phase ratio emulsions (HIPREs)



Objectives and stakes

The final objective is to determine a formulation that optimizes a certain desired controlled release. This comprises the knowledge of the optimal features such as phases in presence, composition, interface type, size and distribution of current objects, phases equilibria, diffusion within phases as well as the evolutionary character of the material.

Main results

- Different non-ionic polymeric surfactants were used to investigate the effect of disperse-phase volume fraction on the rheology and droplet size distribution of oil-in-water highly internal phase ratio emulsions using a semibatch two-step emulsification process. The protocol was appropriate enough to get homogeneous and stable gel-emulsions for more than six months.
- A model associated to percolation theory was tested successfully with the experimental data of previous emulsions giving useful information about processing and structural parameters.
- A programming code was written in order to estimate activity coefficients of liquid-liquid mixtures using the modified UNIFAC (Dortmund, 1993) group-contribution method. An additional code was well prepared for calculating the partition coefficient of a tracer substance within a two liquid-phase system with a surfactant layer in between.
- A first experimental validation part of the predicted partition coefficients is showing good results with the system under study. This tool could be extrapolated to other systems.

Methodology/ Experimental approach

A development of physico-chemical models is required to quantify mass transfer as function of product composition and structural parameters. Expressed as a reverse design problem, appropriate simulation tools (including thermodynamics, mass transfer and formulation) will be developed to rank generated systems versus an optimal target function (zero order release for example). 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 are presented as a relevant model system for the experimental validation of this work.

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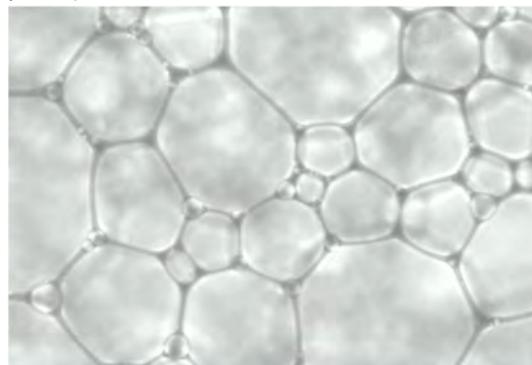
<p>2015</p> 	<p>Etude de la coalescence d'émulsions concentrées via la rhéologie interfacial</p> <p><u>Edeluc López- González (4th year)</u></p> <p>Lionel Choplin, Véronique Sadtler, Dominique Langevin GEMICO</p>	
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General context, scientific issues

Concentrated emulsions are subject of interest in different industrial areas. Despite the active research on emulsions, the role of the surface-active agents remains unclear. It has been postulated that the important parameter affecting emulsion stability is surface rheology, but there are not definitive results [1]. Besides, in the last years there has been an increasing tendency to substitute small molecule surfactants by chemically modified biopolymers to formulate new products like nanoparticles or emulsions [2].

Illustration

(Microscopic photo. Emulsion with 95% internal phase)



Objectives and stakes

- Investigate correlation between the long-term physical stability of concentrated emulsion and interfacial rheological parameters
- Elucidate emulsion destabilization mechanisms following droplet size evolution in well-defined emulsion systems.

Main results

Hydrophobically modified polysaccharides [3] and commercial polymeric surfactants were used to prepare highly concentrated oil-in-water emulsions with volume fraction of dispersed phase going from 0.75 up to 0.95. The emulsions obtained were very stable, without droplet size change and with a storage modulus (G') that remained constant during several months. Comparatively, emulsions were prepared in the same way using molecular surfactant. It has been shown that the strong adsorption of polymeric surfactants at interfaces form thick and viscoelastic adsorbed layers, which provide efficient barriers against coalescence and therefore lead to highly stable oil-in-water emulsions [4]. It was also obtained that shear interfacial viscoelasticity plays a small role on the stabilization, suggesting that emulsion high stability is then attributed to adsorption/desorption phenomena.

Methodology/ Experimental approach

Concentrated emulsions have been prepared following a semi-batch process. These emulsions were obtained varying formulation parameters (dispersed phase fraction, nature of dispersed oil phase, substitution rate of modified polysaccharides). Polymeric and molecular surfactants were used to stabilize oil-in-water emulsions with internal content up to 95%. These surfactants were studied and compared from their interfacial properties, including dynamic interfacial tension, interfacial rheological properties (both, shear and dilatational) as well as intermolecular interactions in solution. Moreover, the emulsions were characterized by determining their average droplet diameter and their rheological in the linear visco-elastic range. Emulsions stability was studied by following up these properties over time.

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2015



nexter
MUNITIONS

Study and modeling of the influence of the physicochemical properties of concentrated suspensions on their rheological behavior

Fabien Sta (2nd year)

Peggy Lamy-Bracq¹, Philippe Marchal², Cécile Lemaitre²

¹Nexter Munitions, ²LRGP - GEMICO



General context, scientific issues

Nexter Munitions is recognized for its studies led in the fields of the melt-cast process [1]. This process consists in obtaining a homogenous biphasic concentrated suspension by mixing a melted fusible 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 fusible explosives rheology. Indeed the rheology of concentrated suspensions is still accurately studied in various industries, because of the rheological complexity of this type of mixture [2].

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 numerical modelling.

Methodology/ Experimental approach

The first step of this work was to establish a rheological methodology to study the suspensions, characterize their rheological behavior and acquire relevant rheological information. The second step consists in validating this methodology, by confronting the obtained results with those acquired via the industrial process. A design of experiments is also conducted, in order to highlight which component(s) is(are) the most discriminating considering the casting of those suspensions.

Finally, the rheology of the mixture will be correlated to the physicochemical properties of their components, in order to be able to model and predict the flowability of those formulations.

Illustration: Industrial casting unit (left) and rheometer (right)



Main results

As stated previously, a rheological program was developed. To validate this program, the rheological/melt-cast process was studied. Four formulations were made and implemented with the rheometer and the industrial plant (in order to assess the shells filling times); the first results showed the sought matching between laboratory and industrial processes. Further experiments, involving repeatability and more different formulations, will be managed to confirm this tendency. This first step also highlighted the fact that the studied mixtures present a rheology which is time dependant, with a marked viscoelastic character.

A design of experiments was also settled (and is still running), to clearly determine which components impact the more the rheology of the fluids. This experimental design is also an opportunity to study the experimental variance of the rheological data. This DOE follows a screening design: sixteen formulations are studied, each being measured ten times to test the repeatability of the method. To quantify this variance, and repeatability, the Relative Standard Deviation is calculated.

The next step is a treatment of the experimental design results, followed by the physicochemical characterisation of the components.

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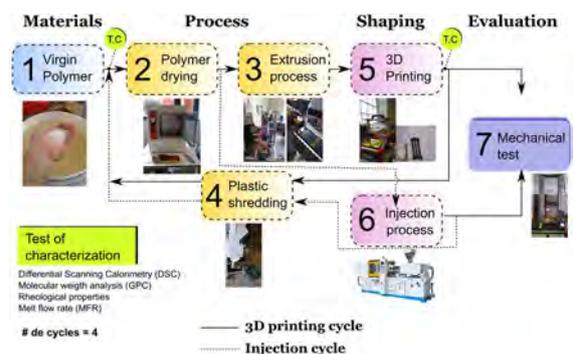
<p>2015</p> 	<p>Recyclability and Additive Manufacturing in an Open source context: Optimization of processes and methods Fabio Alberto CRUZ SANCHEZ (2nd year)</p> <p>Mauricio CAMARGO¹, Hakim BOUDAOU¹, Sandrine HOPPE² ¹Research in Innovation Processes ²Processes for Products and Materials</p>	
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General context, scientific issues

Additive Manufacturing (AM) is defined as a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies like machining.

This thesis is inscribed within the polymer recycling field in the open source additive manufacturing (called *3D printing process*). The overall goal is to have a better understanding on the conditions and scale of the recycling process, and the implications on the diffusion of this growing technology.

Illustration



Objectives and stakes

- Establish the operating conditions for the recycling of PolylacticAcid (PLA) for open source additive manufacturing.
- Characterize the physical properties of the PLA and the corresponding operating conditions.
- Evaluate the structures coupling structural optimization (with 3D printer) and material optimization (with the composite materials created).
- Explore different candidate reinforcing compounds to create composite materials based on the polylactic acid (PLA).
- Propose an open source user environment under which this technology will be adopted

Main results

- Literature review about the AM technology has been done in order to understand operating principles, materials, advantages and disadvantages of each AM process.
- Exploratory experiments have been done at LRGP in order to determine the parameters, conditions, and the first results about the recycling polymer. The polymer used for these first experiments has been recycled polylactic acid from Lorraine Fab Living Lab.
- The first mechanical tests of the PLA using the 3D printing and the injection process have been develop in order to characterize the initial properties.
- The expected main results are the evolution of thermo-mechanical and rheological properties of the polymer in function of the number of recycling cycles (extrusion) in order to evaluate the degradation of the process in the material.

Methodology/ Experimental approach

1. **Development of experimental tests** in order to evaluate the influence of parameters on the quality of products made by recycled materials.
2. **Optimization of operating conditions** to obtain suitable materials for open source AM, and at the same time, to establish minimal requirements to ensure technical quality of the materials.
3. **New structure and material development:** The goal is to explore the feasibility of composite structures with materials issue of PLA. Topological optimization will be achieved with the 3D printing process and material properties optimization with the developed composite material

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2015



Polyethylene blends reinforced with nanometric fillers and tire waste devulcanized by microwaves

DE SOUSA Fabiula

Sandrine HOPPE / Guo-Hua HU/ Carlos SCURACCHIO

Process for Products and Materials
(Polymer Process Engineering)



General context

These last years, the search for solutions to the problem of the elimination of waste polymers, notably waste from tyres, which raise grave environmental problems, knows an increasing development. In this context, this research project has for objective to contribute to the development and the promotion of innovative solutions which appeal to the knowledge developed in the domains of nanotechnologies, as well as the science and engineering of the new materials. More particularly, this study deals with the possibility of valuing waste from tyres by using them as raw material (as agents of reinforcement) for the elaboration of thermoplastic elastomers.

Objectives and stakes

- Increase adhesion between polymer matrix and devulcanized Ground Tyre Rubber (GTR) into the thermoplastic elastomers
- Optimize the operating process conditions of extrusion to obtain efficient dispersion of elastomeric phase into the thermoplastic matrix.

Methodology/ Experimental approach

The work has been carried out following four steps :

- Stage 1: Preparation of nanocomposites, study of the efficiency of GTR devulcanization process adopted and characterization of the phases of the blends
- Stage 2: Analysis of the best processing
- Stage 3: Preparation of polymer blends (using the best processing conditions obtained in the Stage 2) and study of the evolution of the morphology in twin screw
- Stage 4: Characterization of the final properties of the blends.

Illustration

Devulcanization of GTR

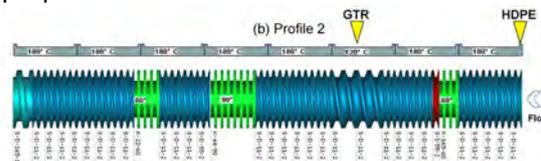
Ground Tyre Rubber (GTR) was devulcanized in a system composed of a conventional microwave oven adapted to a motorized stirring system with speed control.



Microwave oven for devulcanization of GTR

Preparation of blends

Blends of (HDPE/ devulcanized GTR/ organically modified clay Cloisite) were prepared in a twin-screw extruder



Screw profile for the extrusion of HDPE and GTR

Main results

- Viscoelastic properties of blends were analyzed by Dynamic Mechanical Thermal Analysis (DMTA V Rheometric Scientific.) in conditions of dynamically vulcanized blends
- Extrusion operating conditions were optimized to obtain a fine dispersion of GRT inside polyethylene matrix.

References

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2015



In-situ multi-scale monitoring of polymerization using Raman spectroscopy

Elise Dropsit (2nd year)

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Process for Products and Materials



General context, scientific issues

In situ monitoring of emulsion polymerization in reactors covers several challenges such as getting further insight into involved chemical and physico-chemical phenomena, characterizing the reaction medium at various scales (macromolecules, particles...), improving process control.

Recently, we proved that Raman spectroscopy could be a good technique to answer these demand ^{[1], [2]}.

Objectives and stakes

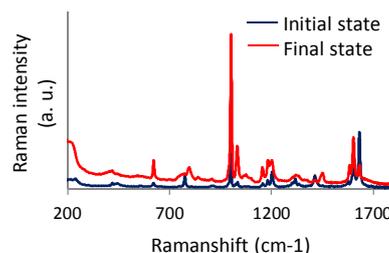
The aim of that work is to demonstrate the capacity of the Raman spectroscopy to control the polymerization of styrene via macro-emulsion process.

Methodology/ Experimental approach

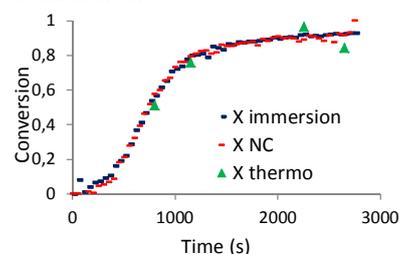
- The synthesis is carried out in a double-jacketed glass reactor under constant temperature and nitrogen atmosphere. The reaction medium is stirred thanks to a magnetic stirrer for spectroscopic measurements.
- Spectroscopic measurements are realized in situ with a RXN2-785 nm Raman spectrometer (Kaiser Optical Systems) equipped with remote and immersion probes.
- The synthesized polystyrene is characterized by thermogravimetry, gas chromatography, diffusion light scattering and absorption measurements.
- Chemical parameters are varied to synthesized polystyrene in different kinetics and with different particle sizes.
- Optical parameters (lens, wavelength...) are varied to understand optical phenomena.

Illustration

- Raman spectra (immersion probe)



- Conversion



Main results

- Reproducible synthesis and stable emulsion were obtained despite the use of a magnetic stirrer.
- Impacts of the chemical parameters on the polymerization kinetic were checked.
- Sensitivity of Raman spectroscopy to variation of polymerization kinetic was proved.
- Good correlation between thermogravimetric and spectroscopic conversion measurements was demonstrated.
- Optic parameters influencing spectroscopic results were detected.

References

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2015



Concept of Reactive Compatibilizer-tracer for Probing Reactive Polymer Blending Processes

Wei Yun Ji (2nd Year)

Guo-Hua HU

Processes for Products and Materials
(Polymer Process Engineering)



General context

Polymer blending has been an efficient route to create new materials that combines the desirable properties of each blend composition without creating new molecules. However, most polymer pairs are thermodynamically immiscible leading to phase-separated blends with poor properties. Therefore, reactive polymer blending involving in situ generation of compatibilizers such as block or graft copolymers provides a convenient method to improve the adhesion of the interfaces and control the morphology of the resulting blends.

It is very challenging to investigate a reactive compatibilization process because both mixing and interfacial reactions between reactive polymers are highly coupled. Most importantly, the amount of the in-situ formed copolymer is often so low that it is very difficult to determine it in a relatively accurate manner, especially for an industrial scale process.

Objectives and stakes

To probe the interfacial reaction and morphology development during the reactive polymer blending by using a reactive compatibilizer-tracer.

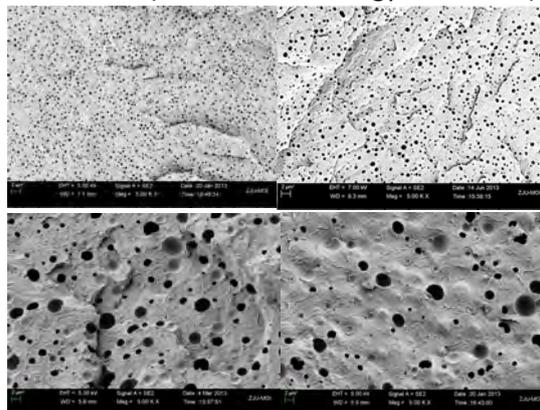
Methodology/ Experimental approach

The mixing of blend components (PS, PA6 and PS-TMI-MAMA) was carried out in a Brabender torque rheometer at different time intervals.

The morphologies of the blends were characterized by a scanning electron microscopy (SEM) of ZEISS ULTRA55.

The reacted PS-TMI-MAMA was measured by via GPC with UV detector.

Illustration (result, methodology or context)



SEM micrographs of reactive compatibilized polymer blend. A: Mixing 2min; B: Mixing 4min; C: Mixing 5min; D: Mixing 10min.

Main results

- The dispersed phase domain size first decreases and then increases with mixing time.
- The reacted PS-TMI-MAMA increases with mixing time.
- In the initial period of mixing, PS-TMI-MAMA reacts with PA6 to form the graft copolymer which could decrease the particle size. As mixing pursues, the graft copolymer becomes comb-like with more PA6 grafts is unstable at the interface and could be pulled out of the interface and move to the PA6 phase. The dispersed phase domains coalescence and increase in size.

References

1. Zhang CL, Feng LF, Hoppe S, Hu GH. *AIChE J.* 2012; 58: 921-1928.
2. Bhadane PA, Tsou AH, Cheng J, and Favis BD. *Macromolecules.* 2008; 41: 7549-7559.
3. Charoensirisomboon P, Inoue T, Weber M. *Polymer* 2000; 41: 6907-6912.

2015 	Design and multi-criteria optimization of an extrusion process for the manufacture of nanocomposites based on recycled polymers reinforced by cellulose nanocrystals Karen Mariana MANCERA GARCIA (2nd year) Sandrine HOPPE ¹ , Fernand PLA ¹ , Vladimir ESCOBAR ² ¹ LRGP UL Nancy, France; ² IPICT, San Luis Potosi, Mexique Processes for Products and Materials	
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General context, scientific issues

This project enters within the framework of the valorization of recycled polymers, which are generally degraded during the processes implemented for their recycling.

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.

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 biodegradability, are very promising candidates for designing new composites.

Objectives and stakes

- CNCs synthesis and surface modification
- Synthesis of a compatibilizer based on SEPS, PAA and CNCs.
- Manufacturing by melt extrusion, of
- recycled reinforced PET/LDPE.

Methodology/ Experimental approach

Two key scientific problems must be solved :

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)

Next work:

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

References

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- 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

CNCs characterization (TEM)



(Aver. length 110-150 nm ; Aver. thickness: 5-8nm)

Synthesis of reinforced nanocomposites



Extrusion and granulation



Injection molding



Blends samples

Main results obtained until now :

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).

2015



Natural fiber composites : Extrusion compounding and characterization

Romain TESSIER (Chercheur contractuel)

Sandrine HOPPE, Guo-Hua HU

Processes for Products and Materials



General context

Composites are a combination of two or more materials yielding properties superior to those of the individual ingredients. Fibers reinforced plastics combine synthetic or natural fibers with thermoset and/or thermoplastic resins. Today, most composites come from petrochemical industry. However, oil reserves are decreasing day by day. To avoid this shortage, one solution consists to replace synthetic fibers by natural fibers.

Industrial hemp fibers are one of the strongest and stiffest available natural fibers and therefore have great potential for use in composite materials. Moreover, these light and cheap fibers have a facility for recycling. That is why hemp fibers compete today with glass fibers in automotive and packaging industry for examples. Nevertheless, the major drawback of natural fibers is their poor affinity with polymer matrix.



Twin-screw extruder (opened barrel)



Pellets of compounds - Dumbbell test specimens

Objectives and stakes

- Increase adhesion between polymer matrix and natural fibers
- Improve composites mechanical properties

Main results

- Different chemical and physical treatments have been tested to modify the fibers/polymer affinity. Some allows increasing mechanical properties of composites (compared to the raw fiber composites).
- Up-scaling from laboratory scale (micro-compounder) to pilot plant (twin-screw extruder) and supplying industrial partners with compounds to make prototype parts.

Methodology/ Experimental approach

To increase adhesion between matrix and fibers, a solution consists to functionalize fiber's surface by chemical and/or physical treatments. A second one is to add to matrix a suitable compatibilizer.

Compounds are produced by extrusion blending of fibers with polymer granules. The pellets were injection-molded into dumbbell-shaped specimens for mechanical tests.

References

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2015



Study of the graft polymerization of styrene onto ground tire rubber powder

Ning YU (4th year)

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Processes for Products and Materials



General context, scientific issues

Rubber is a common material, mainly used in the automotive industry. As a result, large quantities of waste tire rubber are produced every year.^[1] The cross-linked structure of waste tire rubber (also known as ground tire rubber, GTR) along with the presence of stabilizers and other additives, inhibits its degradation process thus resulting in serious environment issues.

A solution to this problem is the re-use of GTR particles in different applications, such as fillers in thermoplastics, elastomers and thermosets.^[2] However, the incorporation of GTR powders into a number of polymer matrices significantly impairs the mechanical properties of the resulting material, even at low rubber content, due to poor adhesion issues between the two materials as well as to the relatively large particle size of GTR.

Objectives and stakes

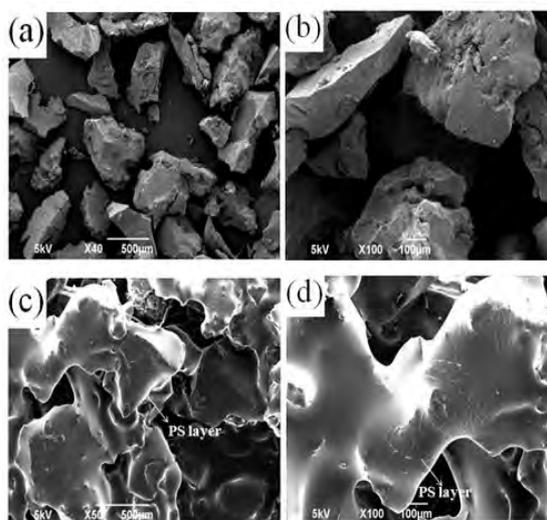
The objective of this work is to study both experimentally and by modelling free-radical grafting polymerization of styrene onto the rubber particles.

Modeling approach

A coupled phenomenological/mechanistic modelling approach is followed for the theoretical study of the complex grafting free-radical polymerization kinetics. Initially, an Artificial Neural Networks (ANN) model is developed to study the influence of the main reaction conditions (i.e., temperature and amounts of monomer, GTR and initiators) on the monomer conversion and grafting efficiency indexes. At a second stage, a comprehensive kinetic model is developed, on the basis of the moments method, that displays extended predictive capabilities.^[3]

Illustration

SEM micrographs of original GTR powders (a and b) and PS-graft-GTR powders(c and d).



Main results

1. The grafting polymerization is successfully carried out in the presence of two different chemical initiators (i.e., BPO and DCP).
2. The grafting efficiency of PS onto the GTR particles is increased with increasing GTR content, decreasing initiator content and increasing ratio of BPO over DCP content.
3. The glass transition temperature, T_g , of PS-graft-GTR is higher than the that of the original GTR.
4. The thermal stability of GTR with the grafted PS chains is significantly higher than that of the original GTR.

References

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