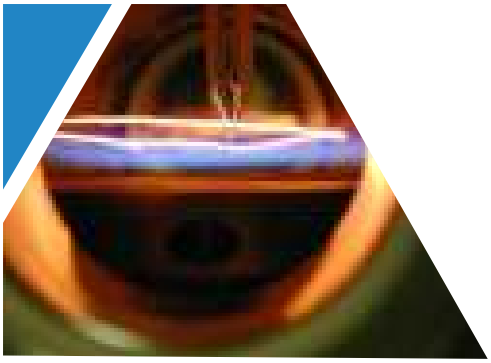
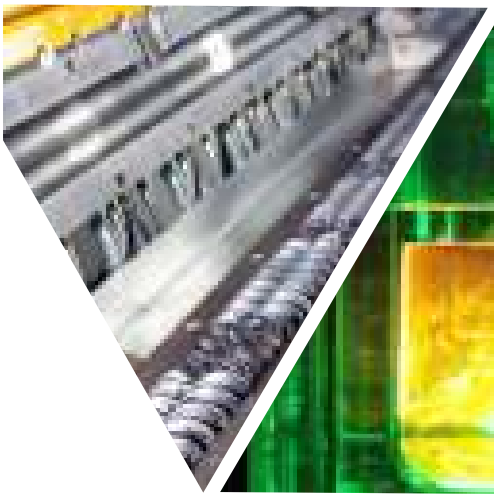
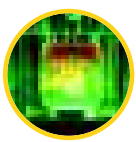




PRESENTATION OF PHD AND POST-DOCTORAL RESEARCH WORKS

2018

REACTIONS AND CHEMICAL ENGINEERING LABORATORY



Presentation of PhD and post-doctoral works at LRGP

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

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

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

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

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

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

INDEX

PerSeVal - PROCESSES FOR ENVIRONNEMENT, SAFETY AND RESOURCE VALORIZATION

PRIMO - INTENSIFICATION, OPTIMIZATION AND ARCHITECTURE OF PROCESSES

PRODUCT ENGINEERING

PERSEVAL

PROCESSES FOR ENVIRONNEMENT, SAFETY AND RESOURCE VALORIZATION

2018

Direct hybridization of a PEM fuel cell to a supercapacitive storage device – Comparative study of the aging in urban cycling mode and optimal management of hydrogen consumption

Divyesh ARORA (2nd year)

Stéphane RAËL, Caroline **BONNET**

Axe PErSeVAL | SYSPOL

Keywords: PEMFC, supercapacitors, direct hybridization, hydrogen saving, dynamic load cycling (FC_DLC)

General context, scientific issues

For transport application, fuel cells (FCs) can be hybridized with supercapacitors (SCs) by means of additional power electronic components (active hybridization) [1] which thereby increases overall cost, weight and introduce additional losses due to an extra level of power conversion.

On the contrary, FC can be connected with SC directly (passive/direct hybridization) [2,3], without any means of external power electronic converters. In this configuration, both devices operate at the same voltage as they are connected in parallel. Thus, SCs can passively provide the peak power requirements under transient load conditions, thereby reduce power losses, weight and cost of the system.

Objectives and stakes

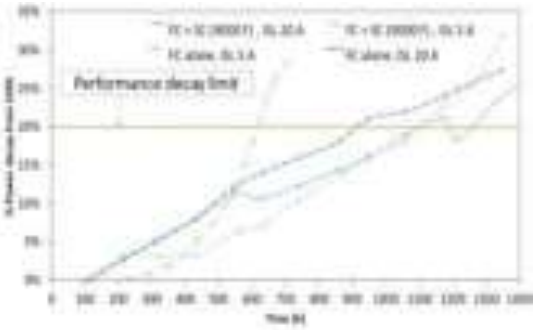
The direct hybridization of a fuel cell to a supercapacitor allows better management of the transients induced by sudden change in the electricity demand, while avoiding the presence of power electronics converters.

The PhD subject proposed is focused on (i) the investigation of the degradation of the fuel cell core (diffusion layers, electrodes, membrane) depending on its hybridization state while operating at FC_DLC mode and (ii) research of the optimal strategy for hydrogen supply to the cell for a given performance.

On hybridized and non-hybridized FCs / Experimental approach

Long term tests were carried out on the home-made test bench, with evaluation of FC components degradation extent and causes (polarization curve, electrochemical impedance spectroscopy, linear and cyclic voltammetry). Furthermore, the control of the hydrogen flow rate is developed for the sake of the minimal hydrogen feed supply. The degradation study has been extended to evaluate the importance of hybridization by varying different strategies of the control of hydrogen flow rate (stoichiometric factor and safety limit current (ISL) corresponding to minimum hydrogen flow rate supplied to the FC). And then compared with the studies of hybridization configurations with non-hybridized FC configuration.

Illustration 1: Durability test on different strategies



Main results

As illustrated above, direct hybridization with supercapacitortors prevents the risk of transient starvation of the fuel cell; thus in hybridized configuration, the over-supply of hydrogen is reduced from 53 % (FC alone) to 29 % (FC hybridized with the stack of supercapacitors of 9000 F) [4,5].

By changing the safety limit current from 20 A to 5 A, the hydrogen over-supply (loss) was reduced to 20 % with the same capacity of supercapacitors hybridized.

The durability of the fuel cell is improved in hybridized mode, since the limit of power loss is attained after 1100 h cycling. The minimum flow rates supplied to the FC are decreased to the sensitivity threshold of the hydrogen flow rate regulator corresponding to a safety limit current equal to 5 A. The lifetime of the FC alone is consistently shortened, 700 h compared to 1400 h for the other strategies. [Illustration 1]. The durability study has been supported with the results of rapid increasing trends of membrane resistances and voltage decay rate.

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2018

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

Nelly Chrystelle Houéfa ATINKPAHOUN (4th year)
Marie-Noëlle PONS, Henri H. SOCLO
Axe PErSeVAL | Sols & Eaux

Keywords: Wastewater treatment ; Variability urban wastewater pollution.

General context, scientific issues

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

Objectives and stakes

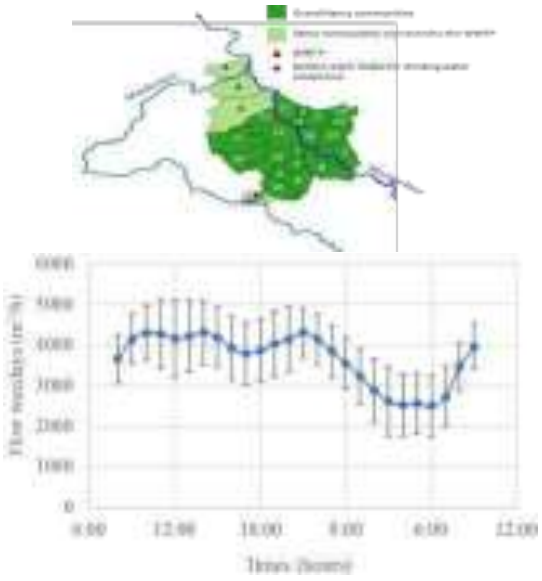
The objectives are to study daily variability of wastewater entering the Maxeville wastewater treatment plant in "Grand-Nancy" in France and of wastewater entering "Vie-Nouvelle" city at Cotonou in Benin. In medium or long term, the experimental data from this study will allow the development of a methodology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

Methodology / Experimental approach

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

COTONOU

GRAND-NANCY



Flow daily variation in "Grand-Nancy"

Main results

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

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

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2018

Metal trace elements and sodium chloride transfer dynamics in water-sediment interface in road retention basin

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Marie-Odile SIMONNOT, Ivana DURICKOVIC (Cerema)...
Axe PErSeVAL | Sols et Eaux | CEREMA

Keywords: Retention pond, NaCl, metal trace elements, solids suspended matter, General context, scientific issue

General context, scientific issues

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

[2]. Therefore, the retention pond only delays the release of sodium chloride and dissolved metals into the environment, affecting ecosystem quality.

Objectives and stakes

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

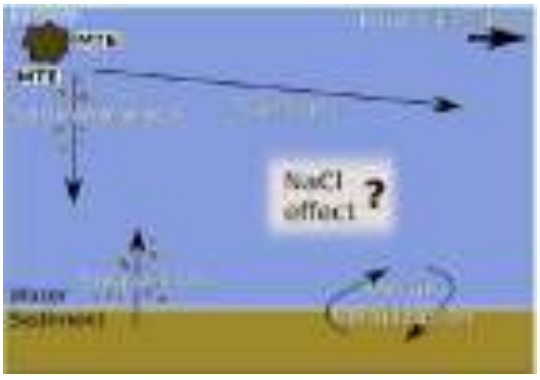
Methodology / Experimental approach

The study focus on monitoring a newretention pond during 2 years. Water and sediment composition was characterized and we looked at concentrations of deicer agents, solid suspended matter (SSM), trace elements and major elements (such as anions, organic matters, cations). This measurements was done during different rain/snow events to comprehend relation between events and NaCl influence.

In order to understand NaCl impact on SSM and its link with trace metals and deicers, the SSM concentration and composition was be monitored at different NaCl concentrations.

Metal distribution in the pond inlet was characterized thanks to analyses of metal concentration on SSM and water and the variation of geochemical balance.

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



Main results

- In the course of the 1st year, the water and sediment characterization had allowed to highlight functioning different between part of basins -including sediment distribution, water flow and water composition.
- During this winter 2016-2017 some results have been obtained on deicer concentration, retention and transfer
- As in the 1st basin [3], the relation betweenchloride concentration and conductivity was established on this new basin.
- The deicer salt collected by basin depend on road design and meteorological conditions
- The deicer salt has a impact on the SSM transport on runoff, so an increase of metals concentration is excepted

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2018

Coupling of bacteria and microalgae for the wastewater treatment and production of valuable biogas sludge

Olfa BEJI (4th year of PhD)

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Axe PErSeVAL | SysPol

Keywords: Multitrophic rotating biofilm contactor, sustainable wastewater treatment, opacity biofilm, microalgae-bacterial flocs

General context, scientific issues

Multitrophic rotating biofilm contactor (MRBC) technology represents a sustainable strategy using microalgae-bacterial flocs (MaB-flocs) within biofilm, where mineralization and photosynthesis are coupled in order to avoid O_2 supply and CO_2 production. In addition, sustainable remediation processes allow a low cost removal of wastewater nutrients and accumulate valuable biomass (for composting or anaerobic digestion) which improves the economic performance of this technology.

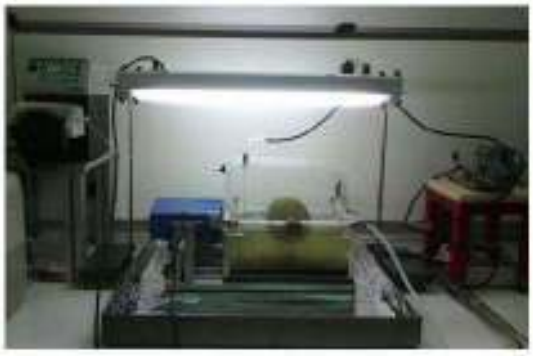
Objectives and stakes

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

Methodology / Experimental approach

A laboratory multitrophic rotating biofilm contactor (MRBC) with a tank volume of 2.5 L was used in this study. Six PVC discs on which the biofilm grew were all identical with diameter of 10 cm and placed on the axle separated by two small rubber spacers of 1 cm. All discs have concentric grooves with dimensions (2x2 mm). The discs rotated at a relatively low speed (10 rpm) to avoid detachment events. Inoculation was carried out in batch mode for 7 days by mixing 800 mL of microalgae-bacterial flocs (MaB-flocs). After 7 days of anaerobic pre-culture of MaB-flocs, the feeding rate was maintained at 2.5 $L.day^{-1}$ of the synthetic wastewater during the anaerobic treatment. The concentration of the feeding solution was fixed to achieve 500 mg of $COD.d^{-1}$ 60 mg of NH^{4+}-$N.L^{-1}$ and 30 mg of PO_4^{3-}-$P.L^{-1}$ under constant supply of light: dark cycles of 16:8h.

Illustration: Image of RBC Reactor Experiment



Main results

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

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2018

MEAClean

Marine BROGAT[1] (Research Engineer)

Cécile Vallières[1], Olivier Potier[2], Léa Sigot[1], Steve Pontvianne[2]

Axe PErSeVAL | SAFE[1] | Sols et Eaux [2]

Keywords: urban runoff, rainwater, trench drain, cleaning system, metals, polycyclic aromatic hydrocarbons (PAHs)

General context, scientific issues

Urban runoff has been identified as a main cause of the environment deterioration. For example, motor vehicle emissions and vehicle tyre wear are some of diffuse sources of chemical contaminants in urban environments. During rainfall, these chemical contaminants are washed from different surfaces such as roofs and roads into the stormwater system [1]. Heavy metals (copper (Cu), lead (Pb) and zinc (Zn)) are of particular concern in such runoff due to their occurence, toxicity to aquatic organisms and persistence in the environment [2].

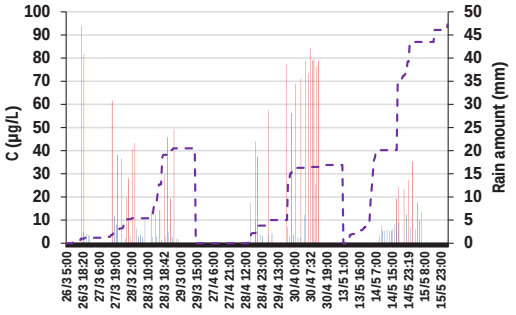
Main objective

The aim of this project is to test an innovative trench drain system with a multi-stage substrate (a white substrate to retain heavy metals and a brown substrate to retaine PAHs) technique to retain pollutants.

Methodology / Experimental approach

The study consists of different tests:
- Under monitored laboratory conditions, equilibrium adsorption (isotherm) studies have been carried out to evaluate the maximum capacity of the white substrate as a sorbent of heavy metals in aqueous solutions using batch contact adsorption mode at different temperatures (12°C and 22°C). In fixed-bed column studies, the breakthrough curves have been studied at different operating conditions such as flow rates. Three metals (copper, zinc and lead) have been selected to carry out these laboratory experiments.
- Characterizations of the 2 substrates have been realized to determine their compositions.
- In pilot plant scale: a trench drain (with and without substrates) has been installed in September 2017 to follow global water quality parameters and retention of pollutants (heavy metals: copper, zinc, lead, nickel, chrome and cadmium; organic pollutants: PAH16; hydrocarbons: hydrocarbon index) under real conditions.

Illustration 1: Concentrations of Zn (II) in runoff water (rain amounts are represented in blue dotted line) before (red bars) and after (blue bars) going through the innovative trench drain



Main results

(1) Effects of contact time and amount of substrate: the removal of copper, zinc and lead by the white substrate reached an equilibrium after 10 days. The effect of amount of substrate on the rate of sorption of heavy metals on this substrate was studied. For a same amount of substrate and same initial metal concentration, the rate of sorption was higher for lead than for copper and zinc. Explanations could be the size of cations and the presence of different phenomena of sorption (adsorption and ion exchange).

(2) Pilot plant scale: Sampling was conducted at irregular intervals during rainfall events. In Illustration 1, a focus on zinc concentration on 3 runoff event samples collected from the trench drain over a period of 3 months is shown. For zinc, the presence of the innovative system allowed a removal efficiency superior to 65% whatever the influent concentration and the intensity of rain event. But for other heavy metals such as copper, the removal efficiencies could be substantially dependent on the influent concentration: higher removal efficiencies were obtained when lower metal influent concentrations were measured.

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2018

Recovery of rare earths from hyperaccumulator plants

Zeinab CHOUR (3rd year)

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Keywords: Rare earth elements, hydrometallurgy, *D.dichotoma*, EDTA, Precipitation.

General Context, scientific issues

Rare earth elements demand has increased over the past years, since they are essential elements for emerging technologies as well as for technologies linked to the transition to a green economy (e.g. permanent magnets, lamp phosphors, rechargeable batteries etc.)[1]. Phytoremediation, defined as the use of plant to remove, immobilize or degrade contaminants, is thought to be a feasible way to decrease the harmless effects of metals in soil and has a great potential for in-situ and low-cost remediation[2].

REEs can be extracted by hyper-accumulator plants and current studies focus on REEs recovery from plants to recycle it.

D. dichotoma, a natural fern growing in acidic soils in Southern China (Jiangxi province), and especially in tailings of former REE mines. This plant is known for its large accumulation capacity of REEs (up to 0.35 %) and also for a high concentration of other metals especially aluminum[3].

Objectives and stakes

- Characterization of biomass
- Process design for REE recovery
- Separation of major REEs

Methodology / Experimental approach

Hyperaccumulator plant used is *Dicranopteris Dichotomas* which has a very strong ability to accumulate REEs.

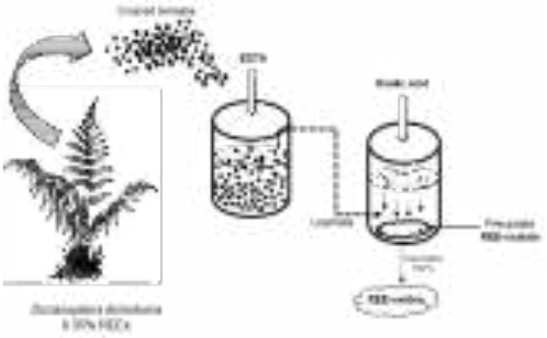
Following approach is adopted:
Determining of the composition of the biomass with digestion

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

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

Elementary composition of biomass is determined by ICP-AES after digestion step (HNO_3/H_2O_2). Solid particles are analyzed by XRD.

Illustration: Extraction process of REEs using EDTA



Main results

Dicranopteris dichotomas can accumulate between 0.17 and 0.38 % of REEs, in majority La, Nd and Ce. The biomass accumulate other metals such as Al (0.25%).

- Biomass leaching with EDTA (0.04 M) leads to extract more than 80% of REEs.

- Precipitation of REE-oxalate is total at pH [2-3] even in presence of EDTA.

- 69 % of REEs present in *D. dichotoma* precipitate after addition of oxalic acid in leachate.

- After calcination of precipitate, the solid obtained contain 80 wt. % of REEs oxides. Major impurities are calcium, aluminum and sodium with 2.3, 1.94 and 1.34 wt. % respectively.

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

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2018

Study of the feasibility of a gas-solid adsorbent for treatment of NOx and CO in the presence of water
Applications to diesel engine exhaust emissions in confined spaces

Florine DELACHAUX (3rd year)

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Axe PErSeVAL | SAFE | INRS/IP

Keywords: gas-solid adsorption, NOx, CO, H_2O, diesel exhaust, zeolite

General context, scientific issues

In France, about 800 000 employees are potentially exposed to diesel exhaust emissions by working in confined spaces like in automotive garages or during the construction and maintenance of tunnels for example. The aim of this project is to remove nitrogen oxides (NOx: NO and NO_2) and carbon monoxide (CO) from the exhaust gas of these non-road mobile machinery. One of the solutions is to use an adsorption process. The main scientific lock is the temperature of the exhaust gas which is unfavorable to the process. The presence of other components such as carbon dioxide (CO_2) and water vapor (H_2O) is also a critical point which can lower the performance of the developed process.

Objectives and stakes

The steps to perform the study are:

- Select some adsorbents able to capture NOx and CO
- Test these adsorbents about pure component adsorption of NO, NO_2, CO and H_2O to find the more efficient
- Choose one adsorbent to study multi-components adsorption with NO, NO_2 and CO in absence or in presence of H_2O at different temperatures

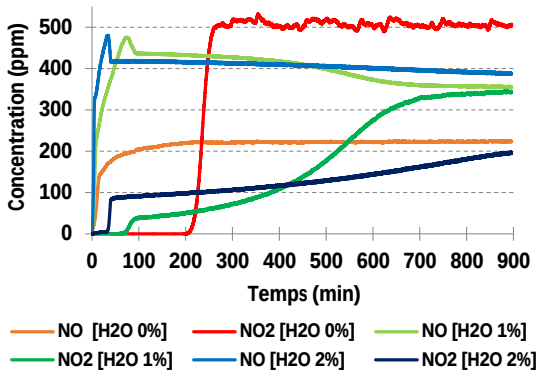
Methodology / Experimental approach

After selecting seven zeolites according to the literature [1-2], the physical structure (surface area and pore size distribution) were obtained by physical adsorption.

Adsorption capacities of each zeolite depend on the structure, on the Si/Al ratio and on the charge-compensating cation. Pure components adsorption permitted to show the influence of these parameters. For adsorption of NO, NO_2 and CO, breakthrough curves were performed whereas isotherms were achieved for CO_2, H_2O and N_2 (used as the inert gas). Isotherms obtained have been modelled with Langmuir, Sips and Toth models. Langmuir best describes the experimental data.

Thanks to these results at ambient temperature, the Na Y 2.55 zeolite was selected to study multi components adsorption with or without H_2O in the gas feed at several temperatures.

Illustration: Effect of H_2O on NO + NO_2 adsorption



Gas mixture: 350 ppm NO, 350 ppm NO_2, 8.5% O_2 and H_2O diluted in N_2 at 30°C

Main results

Breakthrough curves presented above show that, at 30°C, the presence of H_2O in the gas feed modifies NO_2 adsorption. Indeed, the more H_2O is present, the shorter the breakthrough time is and the less the slope of NO_2 is inclined. The last point can be due to the chemical reaction that occurs [1]:

(1) $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

The reaction (1) explains also the formation of NO, that is why NO outlet concentration is higher than NO inlet.

Concerning NO, H_2O in the gas feed does not affect its adsorption but the presence of O_2 in the gas feed leads to the formation of NO_2 [3]:

(2) $2\ NO + O_{2\ gas} \rightarrow 2\ NO + 2\ O^*_{surface} \rightarrow 2\ NO_2$

In presence of H_2O, NO_2 does not seem to be formed that means that H_2O inhibits activation of $O^*_{surface}$.

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2018

Cyanides treatment in gas washing effluents

Alexandre DEMARLE (1st year)

Laurence MUHR, Hervé MUHR

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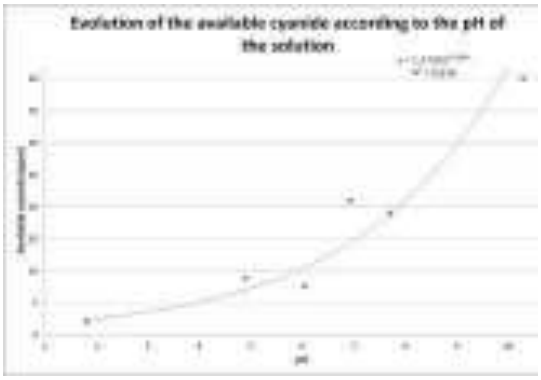
Keywords: Precipitation, cyanides, water treatment, adsorption

General context, scientific issues

In steel industry, metals or alloys are mainly produced by carbothermic **reduction. During this process, cyanides are produced due to the high temperature, and the ore content. The gas coming from the furnace, needs to be cleaned up by washing, thus a part of cyanide are transferred into the water.**

Cyanides are harmful, especially the hydrogen cyanide (HCN). The complex water composition prevents us to use the traditional cyanide treatment [1][2] (well-know in gold industry). A specific treatment has to be developed particularly for steel industry.

Illustration:



Objectives and stakes

The aim of the study is to design a precipitation process for the treatment of cyanide effluents in alkaline environment.

Methodology / Experimental approach

1-Study the iron-cyanide complexes precipitation

-Determination of the operational conditions of ferrocyanide, ferricyanide precipitation. (pH, concentration...)

2-Study of iron-cyanide complexes sorption

-Determination of the most efficient adsorbent
-Study the pH effect on the iron-cyanide complexes sorption.

3-Multi-functionnal reactor sizing to comply with the safety issues

Main results

-Bibliographic research on the operational conditions to form the iron-cyanide complexes, cyanide treatment, and sorption/desorption of iron-complexes.
- Experiments to show the impact of the pH on the cyanide content.

- Highlighting of the competitive sorption of chloride and ferrocyanide

References

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2018

Depollution of waters by electro-coagulation process: Application in Fe containing water potabilisation

Amira DOGGAZ

François LAPICQUE, Marie LE PAGE MOSTEFA
Axe PErSeVAL | SysPol

Keywords: Electro-coagulation, iron, oxidation, precipitation, adsorption

General context, scientific issues

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

Objectives and stakes

The aims of this research are:

- to study the mechanisms involved in the iron removal process by electrocoagulation.
- to evaluate the role of Fe(II) oxidation reaction on iron removal by electrocoagulation.

Methodology / Experimental approach

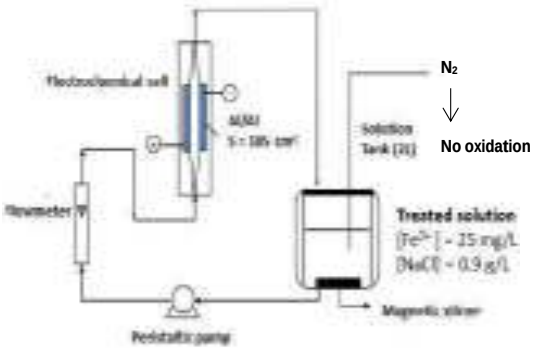
Electrocoagulation experiments were performed in a semi-continuous system operated with flow recirculation of the solution: Al (III) was gradually formed over the run by Al plate dissolution. The electrochemical cell consisted of two parallel plates of aluminum acting as electrodes. The solution to be treated (2 L) was poured into the magnetically stirred tank and continuously circulated in the flow circuit by the peristaltic pump at 200 mL/min. The run was started by introducing iron sulfate in the solution; the current was fixed so that its density was at the desired value, in the range 0.5 -2.5 mA/cm². Each run was performed in 2 environments to evaluate the role of Fe(II) oxidation :

-air oxygen environment

-anoxic environment by nitrogen bubbling

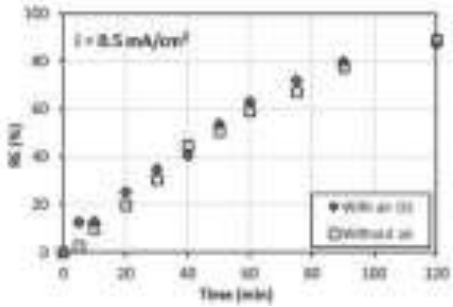
All experiments were conducted at constant temperature (T=25°C) and samples were analysed for Fe^{2+} by 1,10-phenanthroline method (Rodier 1996).

Illustration: Electrocoagulation setup



Main results

Comparison of anoxic and oxygenated environments in iron removal by EC



- The removal yield is little affected by the nature of gaseous environment. Hence, Fe(II) oxidation can be postulated as little significant.
- In a previous study, Fe^{2+} adsorption was shown to have a low contribution in the iron removal mechanism
- $Fe(OH)_2$ precipitation appears to be the predominant phenomenon.

References

[1] Ghosh D., Solanki H., Purkait M.K., Removal of Fe(II) from tap water by electrocoagulation technique, India Journal of Hazardous Materials 155 (2008) 135–143.

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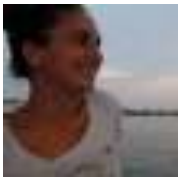
2018

Development of an artificial wetland in Reims for Reclaimed water polishing and stormwater treatment

Maïa DUROZIER (engineer)

Marie-Noëlle PONS

Axe PErSeVAL | Sols & Eaux



Keywords: artificial wetland, downstream of a wastewater treatment plant, treatment of rainwaters, phytopurification, pollutants, monitoring, physical and chemical sensors, chemical analysis

General context, scientific issues

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

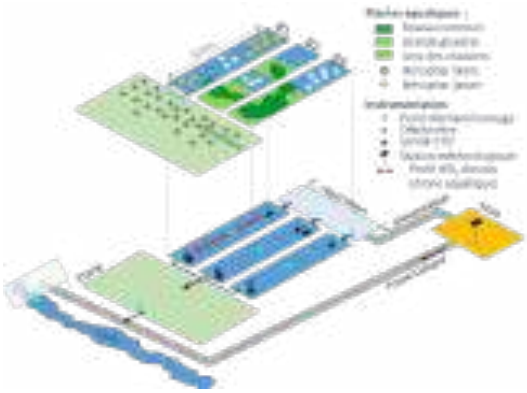
Objectives and stakes

The construction of wetlands to polish the treatment of treated waters is already used in France, but it mainly concerns small wastewater treatment plants. The purpose of AZHUREV project is to build a large-scale demonstration wetland downstream of the Grand Reims wastewater treatment plant (more than 251 000 population equivalent) to provide an improved treatment during dry weather and a treatment of by-passed stormwater. At the same time, this project wishes create habitats for wetland biodiversity. My aim is to monitor the system and its performance in terms of abatement of primary pollution and of some micropollutants for dry and rainy weather and to understand the abatement mechanisms.

Methodology / Experimental approach

The wetland, in water since July 2018, is composed of three ponds (370m long and 50m wide), each with different types of macrophytes and vegetation in various amounts. By dry weather, a percentage of the water treated by the treatment plant is diverted and supplies equally each pond. During rainy events the ponds are supplied by by-passed urban rainwater. At the exit of the ponds, the water passes through a reed bed and a lake before being discharged into a canal that flows downstream into the Vesle River. Flow meters and temperature/conductivity sensors are installed at the entrance and exit of each pond and measure a data every hour and fifteen minutes, respectively. A meteorological station measures air temperature, wind speed and direction, precipitations and PAR. A manual sampling water campaign is conducted monthly for dry weather (sampling strategy, see illustration). Additional sampling campaigns will be organized during the large rain events. With an aquatic drone, water samples are collected in the middle of ponds and dissolved oxygen is measured all along the ponds.

Illustration: Wetland configuration and monitoring scheme and sampling strategy



Parameters measured in water samples are: organic and inorganic carbon, total nitrogen, ammoniacal nitrogen, nitrites, nitrates, o-phosphates, chlorides, sulfates, Ca, K, Mg, Mn, Na, Si, Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, Zn and optical characteristics of organic matter (fluorescence and UV-vis spectroscopy).

Main results

Some defective flow meters and problems of ponds water supply because of vegetation development delayed the monitoring beginning and makes it still incomplete. However, some results are already satisfactory:

- Total nitrogen abatement rates are between 49.7% and 56.2% for winter period, according the pond
- Ammoniacal nitrogen abatement rates are between 60.6% and 72.8% for winter period, depending upon the pond

The system is not enough stabilized to obtain satisfactory abatement rates for others parameters. First sampling for measure of some organic micropollutants (PAH, pharmas, etc.) is planned in August 2018. Wildlife inventory is ongoing but the created wetland has already a positive effect on biodiversity.

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2018

Iron ore treatment by alkaline leaching followed by iron production via alkaline electrolysis

Vincent FEYNEROL (3rd year)

Marie-Noëlle Pons, François Lapicque
Axe PErSeVAL | Sols et Eaux | ArcelorMittal

Keywords: Electrolysis ; Leaching ; suspension ; Chronoamperometry ; Hematite ; Iron ore ; gangue ; Thermodynamics ; ULCOWIN Process ; Ironmaking

General context, scientific issues

To reduce steelmaking CO_2 emissions, ironmaking by low temperature alkaline electrolysis has been investigated the last decades. Although iron production from pure hematite electrolysis is efficiently achieved [1], substitution of hematite with iron ore in the process results in a significant drop in Faradaic yield. One or several compounds in the gangue therefore seem to have a detrimental effect on the electrochemical reduction of iron ore. These compounds must therefore be identified and removed by a purification step prior to the electrolysis.

Objectives and stakes

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

Methodology / Experimental approach

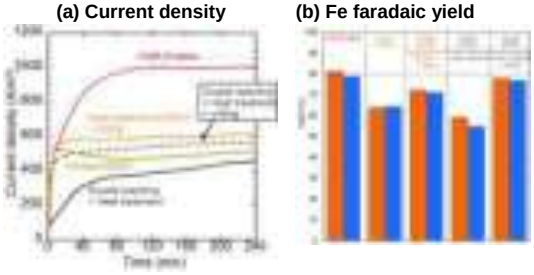
An experimental 4-electrodes setup was designed and built to measure and compare the current density response to the chronoamperometry of ultrafine iron oxides and iron ores, in 50 wt.% NaOH solution, at a fixed voltage of 1.66 V. The setup was airtight and comprised a hydrogen analyser downstream the electrolysis cell, which permitted the deduction of faradaic efficiency, since hydrogen evolution should be the only competitive reaction to iron deposition. The "reactivity" of tested compounds was therefore defined by the intensity of the response current to the fixed potential, and the closeness of faradaic efficiency to 100%.

A leaching setup was also built to conduct selective dissolution experiments in concentrated NaOH solutions of gangue compounds in iron ore such as quartz (SiO2) and gibbsite (Al(OH)3). These leachings were followed by a heat treatment in an oven at 550°C to dehydrate goethite and oxidize magnetite into hematite. Treated iron ores were then submitted to electrolysis to check for any improvement or downgrading of their reactivity.

Illustration

Electrolysis of pure VWR hematite as well as Carajas iron ore (batch M3852) before and after treatments

(a) Current density (b) Fe faradaic yield



Main results

The reactivity of different suspended iron oxides in alkaline electrolysis can be graded as such based on chronoamperometry experiments [2] :
Hematite > Goethite > Magnetite

Suspended hematite based iron ores have decreased reactivity. Iron ores with a higher amount of impurities do not necessarily have the worst reactivity.

Post-treatment milling was found necessary to reobtain the same particle size distribution because of sintering during the heat treatment at 550°C

Elimination of aluminium, goethite and magnetite within an iron ore by alkaline leaching and heat treatment increased its faradaic efficiency by about 15 % but almost did not affect its response current density.

Addition of dissolved $Al(OH)_4^-$ and SiO_3^{2-} to the electrolyte when performing pure hematite electrolysis did not result in faradaic efficiency loss and current density was only slightly decreased.

References

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[2] Feynerol, V., et al. 2017. Reactivity of suspended iron oxide particles in low temperature alkaline electrolysis. Journal of Applied Electrochemistry. 2017, Vol. 47, 12.

2018	Biphasic Aerosols Filtration – Solids Agglomerates and Liquids Droplets (Falbala) Charlotte GODOY (2nd Year) Dominique THOMAS, Augustin CHARVET Axe PErSeVAL | SAFE	

Keywords: Filtration, Soot particles, Droplets, Biphasic aerosols, Fibrous filter

General context, scientific issues

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

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

Objectives and stakes

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

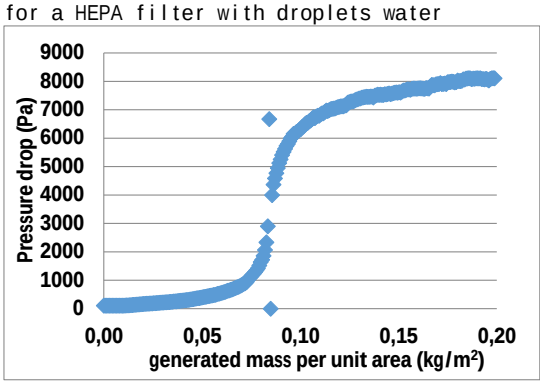
If the filtration of solid or liquid aerosols is relatively well documented in the literature, no study has been interested in the collect of diphasic aerosols.

Methodology / Experimental approach

This thesis work is divided into four steps:

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

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



Main results

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

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

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

2018

Design of innovative processes to produce nickel and cobalt carboxylates after metal extraction form secondary resources by hyperaccumulator plants

Mathilde GUILPAIN (3rd year)

Marie-Odile SIMONNOT, Baptiste LAUBIE
Axe PErSeVAL | Sols et Eaux

Keywords: hydrometallurgy, separation engineering, extraction, hyperaccumulator plant

General context, scientific issues

Agromining is a chain aiming at recovering metals dispersed at low concentrations in soils or secondary resources using hyperaccumulator plants. These plants are able to extract metals from these matrices, and accumulate them, up to a few weight per cents in their aerial parts. Agromining combines plant cultivation and metal recovery by hydrometallurgy [1]. Nickel agromining has been thoroughly studied, and nickel was recovered from the ash, after a combustion stage. The objective of the present research is to develop a new strategy to extract nickel directly from the plant, without burning, and to produce nickel carboxylates, knowing that nickel is mainly complexed by carboxylates in the plant tissues [2].

This work is part of the Agromine ANR program [3].

Objectives and stakes

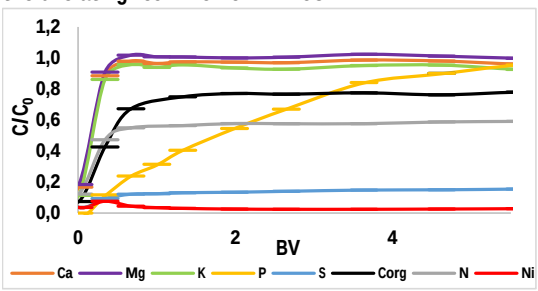
- Determine the best environmental-friendly conditions to extract Ni from several hyperaccumulator plants (the main one being A. murale, by a leaching stage.
- Characterize the leachate (metals, main elements, organic matter) and calculate Ni speciation at thermodynamic equilibrium.
- Optimize the separation of Ni from the other main elements and propose and design processes to recover Ni in the form of carboxylate complexes.

Methodology / Experimental approach

Experiments were performed to optimize the leaching of dry plants with water, in batch and column reactors. The extracts have been characterized by complementary analytical methods (ICP-AES, TOC meter, HPLC, HPLC MS) to monitor metals, organic matter, carboxylic acids and amino acids. Ni speciation has been determined from these results, using Jchess software (thermodynamic equilibria in aqueous solutions).

Different types of separation unit operations have been studied in order to separate Ni in valuable chemical forms, mainly selective precipitation and adsorption on a Ni chelating resin.

Illustration: Breakthrough curves during Ni loading in the chelating resin Dowex M4195



Main results

- 80% of nickel is extracted from the dry plant Alyssum murale by water leaching at room temperature (20 °C) in a packed bed column, leading to a leach liquor containing 10 mM Ni.
- Extracts also contain K (25 mM), Mg (9 mM) and Ca (8 mM), anions, and a diversity of organic compounds.
- 14 % of organic matter is identified being low molecular weight carboxylic acids, mainly malate.
- The calculations run with JChess have shown that Ni is mainly complexed by low molecular weight carboxylic acids.
- Selective precipitation with hydroxide has failed to precipitate Ni hydroxide, despite the results of the predictive calculations.
- These results suggest that Ni is bound to a stronger ligand than carboxylic acids.
- Resin Dowex M4195 enables is to retain the quasi-totality of Ni, which can be then recovered as Ni oxalate.
- Work is ongoing to investigate the feasibility of the use of this resin.

References

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[3] www.agromine.org, seen on May, 18 2018

2018

Elimination of micropollutants in wastewater treatment plants – the effect of the biological reactor configuration on the elimination of micropollutants

Rana HATOUM

Olivier POTIER[1], Harald Horn[2], Joumana TOUFAILY[3], Thibault ROQUES-CARMES[1]
Axe PErSeVAL | Sols et Eaux 1| Karlruhe Institut für Technologie[2]| Université Libanaise[3]

Keywords: micropollutants, Sequencing Batch Reactor (SBR), activated sludge, Sludge Retention Time (SRT); Hydraulic Retention Time (HRT), hydrodynamics

General context, scientific issues

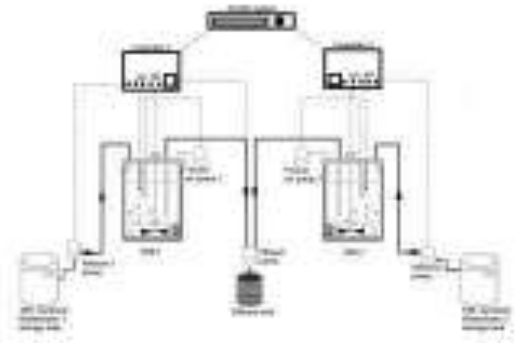
The presence of micropollutants (MPs) in aquatic environment has been intensively studied already for three decades, showing the size and the importance of the problem. Thousands of compounds of anthropogenic origin, such as pharmaceuticals, personal care products, endocrine-disrupting compounds, industrial chemicals, flame-retardants etc., are released from wastewater treatment plants (WWTPs) operated, in most of the cases, with the conventional activated sludge (CAS) system. Unfortunately, due to the design of WWTP and current operation modes, as well as due to the physical-chemical properties of MPs, a complete removal of these problematic substances is not achieved. As a result, the MPs residuals are discharged with the WWTP's effluent to natural environment. It has been already proven, that though the MPs are detected in natural environment in ng/L-µg/L concentration range, this is enough to disturb natural balance, causing even a potential danger towards human.

Objectives and stakes

The aim of this project is to investigate the relation between the operational parameters (such as the sludge retention time SRT and the hydraulic retention time HRT) of biological treatment and degradation efficiency of some selected micropollutants (Benzotriazol, Sulfametoxazole, Erythromycin, Roxithromycin, Carbamazepine and Diclofenac). Biological experiments are carried out in Germany at the KIT (Karlsruhe).

Methodology / Experimental approach

Activated sludge used in the experiments are withdrawn from local municipal wastewater treatment plant - Bruchsal WWTP and used in two Sequencing Batch Reactors (SBR) characterized by two different SRT- 3 d and 10 d. The reactors are operated simultaneously. Following hydraulic retention times are tested – 4 h, 8 h and 12 h. For each combination of SRT and HRT, the kinetics of micropollutants are tested and obtained results are discussed with regard to SRT. Additionally the general performance of the reactors, such as oxidation of ammonia and COD removal, are assessed over different HRTs. Total chemical oxygen demand (CODT, mg/L), nitrate nitrogen (NO_3^--N, mg/L), ammonium nitrogen (NH_4^+-N, mg/L) and phosphate phosphorus (PO_4^{3-}-P, mg/L) are daily determined in influent and effluent using commercial photochemical test. During kinetic experiments, the collected samples are analysed using LC-MS/MS



Main results

Degradation rate constant (L g^{-1}TSS min^{-1})

	SRT = 3 days			SRT = 10 days		
HRT	4 h	8 h	12 h	4 h	8 h	12 h
BZT	0.002	0.001	0.002	0.004	0.001	0.004
ERY	0.004	0.003	0.003	0.003	0.001	0.001
ROX	0.008	-	0.002	0.003	-	0.001
CBZ	0.0008	0.0003	0.0005	0.0007	0.0002	0.0004
DFC	0.0009	0.0003	0.0002	0.0003	0.0003	0.0002

Table. Degradation rate constant (L g^{-1}TSS min^{-1}) of investigated micropollutants determined at different HRTs for SRTs of 3 d and 10 d.

Based on the values of degradation rate constants (Table), no clear dependence between MPs removal and SRT was observed. For instance SRT of 10 d resulted in higher elimination of BZT and SMX ($k_{3d} < k_{10d}$), whereas for other MPs there is no much difference. An increase of HRT from 4 h to 12 h improved slightly the degradation of BZT and SMX only.

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2018

Innovative and continuous production of monoclonal antibodies with sequential multicolumn chromatography

Nicolas-Julian HILBOLD (4th year)

Laurence MUHR

Axe PErSeVAL | Sols et Eaux | Novasep Process SAS | Merck KGaA

Keywords: Monoclonal antibodies, continuous processing, multi-column chromatography

General context, scientific issues

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

Objectives and stakes

Develop an industrial optimized sequential chromatography process based on the SMCC technology for the purification of mAbs.

Design a new equipment meeting the specifications highlighted by the previous steps

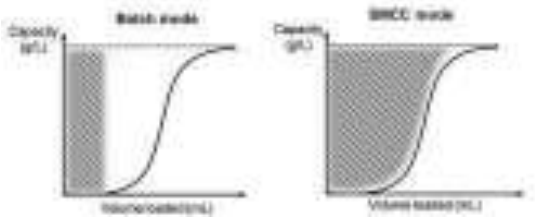
Methodology / Experimental approach

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

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

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

Illustration: Breakthrough curves illustrating the difference in resin utilization between for batch chromatography and SMCC.



Main results

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 research work began in 2015 and ends in 2018. The main outcomes include:

- the design of a development methodology at lab scale, combined with simulation approaches to define the most efficient recipe,
- a comparison of the SMCC and paralle process has been made theoretically and experimentally showing that both processes are interesting depending on the final objectives,
- multi-column processes have been tested for several unit operations in the typical mAb manufacturing process with promising results,
- a pilot-scale equipment has been tested as well, demonstrating good robustness and excellent performance.

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2018

Flow field investigation of high solid anaerobic digestion by Particle Image Velocimetry (PIV)

Yuying HU (3rd year)

Huai-Zhi LI, Souhila PONCIN, Jing WU

Axe PErSeVAL | SysPol

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

General context, scientific issues

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

Objectives and stakes

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

Methodology / Experimental approach

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

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

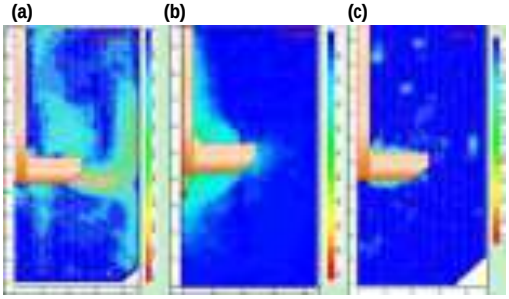
The experimental set-up is illustrated in Fig. 1(a). The impeller (Fig. 1(b)) used in this study was printed via a 3D printer. It was derived from the standard C200 impeller, and its diameter was 50 mm.

(a) (b)

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

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

(a) (b) (c)



Main results

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

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2018

Hydrodynamics in industrial plants cooling circuits: influence on fouling phenomena, characterisation and compartmental modelling

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Keywords: Hydrodynamics, Cooling circuits, Fouling phenomena, Compartmental modelling, Experimental characterisation

General context, scientific issues

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

Objectives and stakes

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

Methodology / Experimental approach

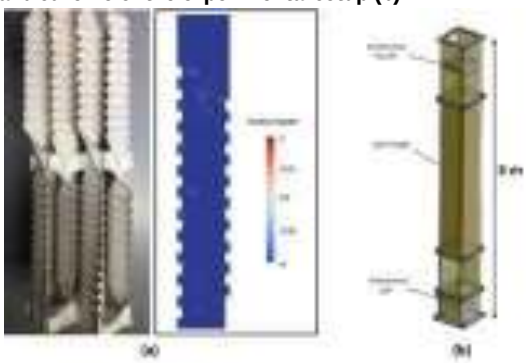
The work methodology can be divided in three main steps.

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

The second step consists in the model construction. The choice of compartmental modelling is justified by the bibliography study: the new compartmental construction method is developed studying previous works from literature and a critical review is necessary. Physical, chemical and biological phenomena are investigated independently in order to identify representative parameters. Then, a global scheme of phenomena interdependence will be built as a shape of the compartmental modelling organisation.

The third step gathers theoretical, simulated and experimental data to develop a global construction method for the compartment modelling of the cooling circuit. Finally, the model must be validated using different information and different sets of data.

Illustration: CFD simulations liquid flow in packing (a) and scheme of the experimental setup (b)



Main results

The study of previous works [1,2] and available data allowed the identification of cooling towers as the most complex part of the cooling circuit concerning hydrodynamic behaviour. Liquid flow in the cooling tower packing has to be characterized.

To obtain local information about the hydrodynamics of counter currant cooling towers, two methods were chosen: experimental characterization and CFD simulations. CFD simulations were performed with the NEPTUNE_CFD code. The CAO of the complex packing structure was designed and the simulations were run for one kind of packing (illustration (a)). The results of the simulations shown that the water film behaviour on packing walls can be predicted with CFD simulations but the results remains far from reality and the code must be improved concerning surface tension modelling.

Experimental characterization is complementary to simulations. An experimental pilot plant was designed and built by the LRGP Atelier and SIEL (illustration (b)). This experimental device was designed to allow visualisation of the water flow, especially the water film thickness, with high-speed camera and endoscopic vision [3].

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2018

Study of sorption mechanisms of water on aerosols issued from fire : identification of the influencing physico-chemical parameters

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

General context, scientific issues

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

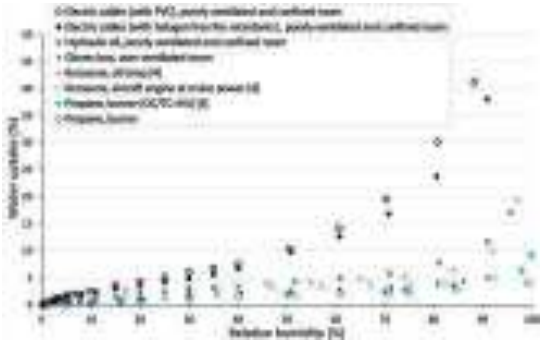
Objectives and taskes

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

Methodology / Experimental approach

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

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



Main results

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

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2018

Origin, behavior and fate of Rare Earth Elements in wastewater treatment plants

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Keywords: Rare Earth Elements, wastewater treatment plant, anthropogenic REEs anomaly, element partitioning

General context, scientific issues

Rare Earth Elements (REEs) have wide and growing applications in high efficiency electronics, energy technologies and/or medical applications. These anthropogenic uses already disrupted the biological cycle of REEs, and lead to enrichments of La, Ce, Sm, and Gd in waters. One of the main pathways for the anthropic REEs to enter in the aquatic systems is effluent from urban wastewater treatment plants (WWTPs)[1].

Objectives and stakes

- Identify and quantify the REEs in influents and effluents of two WWTPs (WWTP of Grand Nancy, France, and WWTP of Schifflange, Luxembourg) and of the artificial wetland of Reims, France.
- Determine the REEs origins (hospitals, industries, etc.)
- Know the REEs variations and fluxes over time (days, weeks, season) and during treatment steps.
- Study the REEs fractionation between the different phases (particular, colloidal and dissolved) inside wastewater.

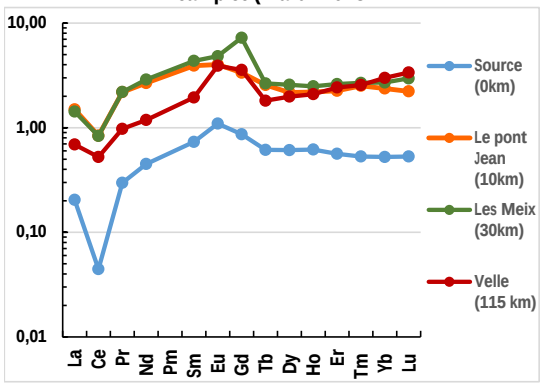
Methodology / Experimental approach

Different campaigns will be conducted:

- Campaigns on Moselle River (France) to determine the quantity of REE and to detect potential anomalies. In fact, Moselle River is used by Grand Nancy metropole to produce drinking water which ends up in wastewater after use. Drinking water will be investigated too.
- Campaigns into the WWTPs using automatic samplers for influents, effluents and some other points during treatment phases. These campaigns will be planned during dry weather events to estimate REEs fluxes for each day of a typical week.

After the campaigns, samples will be filtered at 0.45µm, acidified at 1% with ultrapure HNO3 and then analyzed for REEs by ICP-MS. All filtration and washing protocols will be tested before sampling campaigns and analyses.

Illustration: PASS normalized REE patterns of Moselle samples (March 2018



Main results

Bibliographic researches show that first REEs anomalies in natural water were found in the 90's, for Gd[2]; and that this anomaly has an anthropogenic source (complexed organic Gd used in MRI images). Since, Gd positive anomaly has been reported widely, and other positives anomalies has been discovered, like Sm or La anomalies[3].

One campaign on Moselle River was realized, with 30 sampling stations. Drinking water of Nancy was also analyzed. REEs normalized patterns point out different results:

- Negative Ce anomalies due to the redox behavior of Ce
- Positive Eu anomalies because of the Vosges lithology,
- Small positive Gd anomalies (from 1.5 to 2.7),
- Enhancement of the positive Gd anomaly in drinking water because of the removing of some REEs during the treatment steps.

Compared to some results obtained in 2017, the positive Gd anomalies in 2018 were lower: it can be explain by the higher flow in 2018 than in 2017 (dilution effects).

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2018

Valorization of iron-rich tailings from mining industry. Design and development of a process for the production of electrolytic iron from complex matrices

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Keywords: Red mud, electrolytic iron, electrowinning, sodium hydroxide, alumina.

General context, scientific issues

Industrial ore beneficiation processes generate huge quantities of polymetallic waste often containing iron, like in alumina industry for example. Red mud is the solid waste product of Bayer process for the production of alumina from bauxite ores, it is mainly composed of hematite about 50 wt. % **[1,2]. There are several studies that deal with the benefication of these residues, but, to our knowledge, no works have been published on the valuation of mining residues by electro-deposition, the subject of this thesis.**

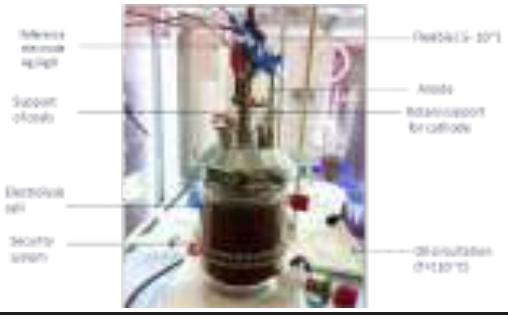
Objectives and stakes

This research topic was developed in order to valorize iron-rich mine tailings by an electrochemical process. The method consists (figure 1) in electroplating, on an electrode, the iron initially dissolved or suspended in an ionic solution (electrolyte) under the action of an electric current. The main objectives are to: (i) produce electrolytic iron, and thus create added value (ii) reduce the volumes of waste, (iii) allow access to other metals contained in the residues (for example titanium), (iv) study the possibility of the re-use of residues depleted in heavy metals for other applications such as road construction or cement manufacturing .

Methodology / Experimental approach

The approach followed can be divided into four phases: (i) study of the influence of current density and the impurities present in the bauxite residues on the electrolysis of iron in standard electrolysis reactor, (ii) development of a protocol allowing the extraction of the impurities responsible for this drop in faradic yields or at least to limit their effects on faradic yield, (iii) optimization of the tests by varying the operating parameters and on the design/geometry of the electrolytic cells, (iv) design, study and optimization, probably using modeling tools validated by experiments, of a pilot unit. Its operation will be optimized by using process parameters such as recirculation loops, flow rates and the applied current. During this first year, we worked on bauxite residues, red mud, based on studies of iron electrodeposition from hematite [3].

Illustration: Figure 1: Experimental set-up



Main results

To understand the effect of current on faradaic yields, electrowinning was carried out at 300 A/m²; 600 A/cm² and at 1000 A/cm².The experimental results of electroplating iron from hematite and bauxaline* are shown in the figure below. These results show that the faradic yield increases as a function of the density of the current. the low yield obtained in the case of bauxaline is explained by the presence of impurities.

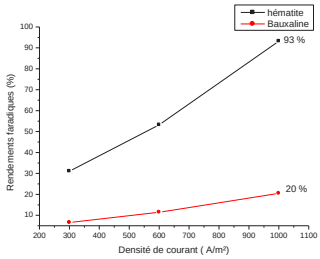


Figure 2: Faradic yields vs. current density in a suspension 12.5M NaOH-hematite (black curve) and 12.5M NaOH-bauxaline* (red curve) for a solid / liquid ratio mass of 1/3 at 110 °C.

ICP-AES analysis of the deposit showed that the product obtained has a purity higher than 96 %.

***** solid residue washed and dried from the Bayer process

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2018

Characterisation of gas transport phenomena through a gas diffusion layer in a membrane fuel cell

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Keywords: Proton exchange membrane fuel cell (PEMFC), Mass transport, Gas diffusion layer (GDL), Through-plane Gas permeability

General context, scientific issues

Proton exchange membrane fuel cells (PEMFC) also called, as polymer electrolyte membrane fuel cell are emerging energy devices for the future, which leverages its technology from the fundamentals of energy conversion and electrochemical systems. The gas diffusion layer (GDL) is an integral part of PEMFC, which is an electrically and thermally conductive porous layer placed between the catalyst layer and the bipolar plates. GDL facilitates access to the reacting gases in diffusing from the bipolar plate channels to the catalytic site [1]. Gas transport through the GDL is a combination of in plane and through plane transport. Effective gas transport depends on a number of factors like type and properties of GDL, compression in the cell, design of bipolar plates to name a few. However, for cell operation the challenge of reaching greater working efficiency persists, and needs to be meticulously addressed by optimising the transport factors [2-3].

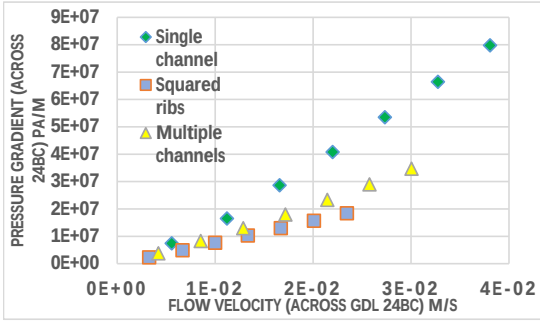
Objectives and stakes

The transport phenomena in PEMFC are usually characterised by gas diffusion and permeability within the GDL porous layers.
The present investigation as a part of PhD deals with validating an experimental technique for which measurements are to be carried out in a dedicated cell using SIGRACET 24 BC and 24 BA as GDL. Comparable measurements are to be carried out on real fuel cells, and results are aimed to correspond to real transport phenomena in GDL, thereby allowing empirical transport laws to be established.

Methodology / Experimental approach

In pursuit of validating the experimental approach, dry gas is used for measuring through plane gas permeability. The working conditions for all had an active surface area of 25 cm sq. with temperature ranging between 20-26°C and nitrogen as dry gas. Additional measuring instruments included pressure sensor and indicator, mass flow controller, and gas flow calibrator. The area of the bipolar plates, nature of commercial GDL, and the flow pattern (single serpentine channel, multiple serpentine channels, square ribs with gas circulation around) have been varied. Gas permeability has been measured in selected systems. Firstly, the measurements were aimed without the GDL, from which the variation of the pressure drop versus the flow rate of permeating gas were to be noted. Further, similar measurements were intended by placing the GDL between the plates, and observing the pressure drops at varied flow rates. The obtained data would suffice for calculating the viscous permeability and inertial permeability using the Darcy-Forchheimer equation for viscous and inertial flow. When Darcy's law alone is incapable to account for the inertial flow, like in case of single channel and multiple channels, Forchheimer term is added to the Darcy's equation [4]. SGL 24BC comprises of microporous layer (MPL) and macroporous layer (MPS) which is actually 24 BA. Hence, for determining the permeability values separately for MPL of 24BC, the resistance related to the MPL of 24BC was deduced from the overall through plane pressure drop of 24BC subtracted by overall through plane pressure drop of 24BA. This enabled to obtain a pressure drop profile explicitly for the MPL at designated mass flow rates.

Illustration: Experimental data of pressure drop versus flow velocity in 3 cells for SGL 24BC tested at 3.5Nm.



Main results

Reporting specifically at 3.5Nm compression on GDL, for 24BC the viscous permeability were in the range of (1.38-2.50) $x10^{-14}$ (m^2) and inertial permeability in the range of (1.10-2.81) $x10^{-10}$ (m) having fair agreement with literature. For 24BA, which only has MPS, the viscous permeability was in the range of (1.58-3.89) $x10^{-13}$ (m^2) and inertial permeability in the range of (1.83-1.90) $x10^{-10}$(m). The viscous permeability value for the MPL of 24 BC was found to be 2.67 x 10^{-15}(m^2) and inertial permeability 1.39 x 10^{-11} (m).

Future Work

i) Estimation of in-plane permeability following similar technique by using the in-house designed fundamental cell device, ii) comparison of fundamental in plane and through plane permeability, and iii) effect of compression on GDL .

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2018

Study of the mechanisms about formation of particles depositions applied to HEPA filtration

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Keywords: Nanoparticles – Pressure drop – Peclet number – Porosity – Cake – Aggregates -

General context, scientific issues

High Efficiency Particulate Air (HEPA) filtration is a key point for the safety of workers and environment. For this reason, the French Institute for Radiological Protection and Nuclear Safety (Institut de Radioprotection et de Sûreté Nucléaire) and the Reactions and Chemical Engineering Laboratory (Laboratoire Réactions et Génie des Procédés) conduct research programs on those containment devices in order to anticipate their behavior especially in case of fire, the most probable incident. The recent works lead to a phenomenological model of clogging[1,3] in which one of the most sensitive input parameters is the cake porosity. The prediction of this porosity for nanostructured particles (soot particles) is a key point to make this model fully predictive.

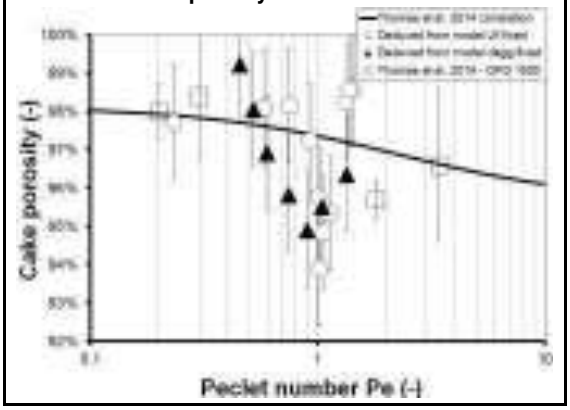
Objectives and stakes

During the filtration process, the porosity of the particle deposit (i.e. "soot cake") formed on the surface of the medium depends on the filtration conditions and particle morphological properties. The structure of the deposit may influence the evolution of pressure drop. The aim of this work is to quantify the influence of each parameter. To do so, analytical experiments based on the variation of aeraulic parameters, the medium, the characteristics of the particles are carried on. Then, the relation deduced from those experiments will be transposed to the case of a full scale HEPA filter.

Methodology / Experimental approach

Till now, the experimental setup is based on a laboratory device producing carbon nanoparticle aggregates. PTFE membranes have been used as filtration media since the penetration of particles inside this media is limited. Experiments have been conducted for different filtration velocities and different particle diameters. To continuously measure the porosity of the deposit of particles, an original device, called MEGAPAN has been developed based on a laser trigonometric method[2]. The porosity has been also deduced from pressure drop values using Thomas model[3]. In parallel, the phenomenology of the cake building will be investigated based on numerical tools.

Illustration: Cake porosity versus Peclet number



Main results

Illustration shows the porosities values obtained with the GFG-1000 generator as a function of the Peclet number. Results show that the trend observed by Thomas *et al.*[3] is globally confirmed. However, for a Peclet number in the 0,7-1 range, porosity values are lower than expected. All this points present the same tendency : a “V” shaped curve. Minimum cake porosity of 96% is then reported for a Pe close to 0.9. This trend still need to be explained on the basis of the particle properties measured by performing additional measurements for other type of nanoparticle aggregates like soot particles or during realistic fires.

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2018

Better understanding of nanoparticle specificities to develop comprehensive modeling approach for nanodust explosions

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Keywords: Dust explosions, nanoparticles, agglomeration, flame velocity, 20L sphere

General context, scientific issues

The nanotechnology sector is growing fast and risk management of nanomaterials has become crucial. In order to predict explosion scenarios of combustible nanoparticles and to be able to design adequate protective systems, it is necessary to model reliably the phenomena to assess risks in a relevant manner [1]. However, the current tools and methodologies do not completely allow to model flame propagation in a nanodust cloud and then to predict explosion consequences from the knowledge of safety parameters.

Objectives and stakes

The objective of this thesis is to determine the influence of surface properties of nanoparticles on the level of dispersability of nanopowders, turbulence level of the cloud and heat and mass transfer within the dust cloud as well as the oxidation kinetic of nanoparticles.

Methodology / Experimental approach

Three types of powders have been chosen for this work: carbonaceous (carbon black), metallic (aluminum) and organic (nanocellulose). A characterization of surface properties of the powder and of their cloud is first realized (specific surface area, time evolution of the particle size distribution).

The explosion severity of nanopowders is studied by measuring the maximum overpressure, the maximum rate of pressure rise and the front flame velocity. A 20 liters explosion sphere is used in order to determine the evolution of the two first parameters as a function of the dispersion system [2], the particle size distribution, the water activity of the powder, the ignition energy and the cold turbulence (measured by Particle Image Velocimetry). The combustion gases are analyzed by micro-chromatography.

The flame velocity is measured in a semi-open tube, in which an air pulse generates dust clouds. A high-speed video camera is used to record the flame propagation. The laminar flame velocity is approximated by taking the flame stretching into account.

A 1D flame propagation model will be developed and validated using the experimental results.

Illustration: Experimental setup for the measurement of the particle size distribution of the dust cloud after dispersion and for cold turbulence characterization.

Main results

It appears that the particle size distribution (PSD) of the nanoparticles before and after injection within the 20L sphere are greatly different and that modifications in the dispersion procedure can impact the fragmentation of the nanoparticle agglomerates. Even slight changes in the PSD of a nanoparticles cloud lead to significant modifications of its explosivity.

On the other hand, turbulence plays an important role in the cloud uniformity and in the local variations in dust concentrations. The ignition time has a direct influence on the turbulence level within the sphere at the time of the explosion, but also on the PSD, since the injection has to be over before the ignition.

In the case of aluminum, pre-ignition has been observed before the injection. To avoid this phenomenon, injection has been performed with pure nitrogen, which seems to be efficient but significantly increases the severity of the explosion.

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2018

Gas-liquid hydrodynamics in a transparent Sulzer static mixer SMX

Marco SCALA (2nd year)

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Keywords: Sulzer static mixer SMX, Shadowgraphy, G-L Dispersion, Particle Image Velocimetry, Hydrodynamics.

General context, scientific issues

For decades, especially for gas liquid dispersions, one of the most popular ideas in the literature is that stirred tanks and bubble columns are the most suitable and efficient devices to achieve the required mixing. But, recent theoretical developments have revealed that the same results can be obtained using different devices, such as static mixers. This device is a mixing equipment inlaid into a housing or pipeline for the blending of fluids flows.

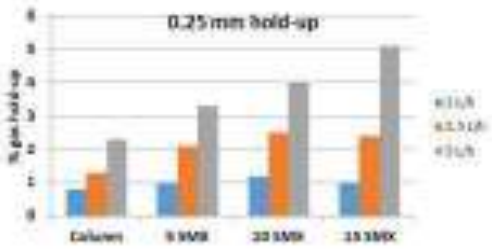
Objectives and stakes

The static mixer has been deeply examined during the last decades starting from the work of Grace [1] and continuing with the research of many authors such as Li et al. [2], Fradette et al. [3]. These papers are just some among the hundreds of references who addressed this topic. Unfortunately, the research on hydrodynamics inside static mixers remains limited. There are key questions and notions that are still not well discussed in the literature such as the behavior of the static mixer when the liquid is stationary and there are gas bubbles rising through it. The ultimate goal of the present study is to answer to the following questions: Can a static mixer represent an alternative to a stirred tank or a bubble column? Can this device ensure a good mixing between a rising gas and a stagnant liquid?

Methodology / Experimental approach

For this study, it was of interest to investigate the static mixer under different points of views. The particle image velocimetry (PIV), the shadowgraphy, the mass transfer and gas hold-up estimation have been performed and exanimated on the SMX static mixer to get an overview on the mixing efficient and on the hydrodynamics into the device. All the experiments have been performed in two different cylindrical columns that are placed inside a square section box filled with the same liquid as that inside the column. This technique avoids any light diffraction and image distortion. Five different SMX static mixer lengths have been employed, with 1, 2, 5, 10 and 15 elements.

Illustration: Nitrogen hold-up in normal-heptane.



Main results

The analysis of the hold-up in aqueous solutions leads to this conclusions: the SMX is more performant in pure water. The higher hold-up reached in such systems is mainly due to bubbles stuck on the SMX surface. By adding SDS at a concentration up to 3%, the quantity of bubbles trapped is negligible and the hold-up decreases. Anyway, the SMX ensures a substantial increase of hold-up. The experiments performed in heptane lead to same conclusion. The mass transfer results do not allow accurate estimation, but they can provide a qualitative tendency: the SMX causes a clear change in the absorption capacity of the system. The flow field results obtained by the PIV show a decrease of the axial liquid velocities inside the mixer in favor of the radial velocities for both the liquids examined. The bubbles rise individually in the SMX. This behavior leads to the formation of preferential paths which have also been confirmed by the shadowgraphy results. In addition, the shadowgraphy analysis in the aqueous systems suggests an important observation: the metallic SMX static mixer promotes the bubble breakup more than the plastic one. This characteristic enables to obtain smaller bubble at the outlet of the metallic mixer inducing a better dispersion efficiency.

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2018

Granular bed filtration for the determination of particle size distribution

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Keywords: Particle size distribution, Nanoparticles, Granular bed, Collection efficiency

General context, scientific issues

Characterization of nanoparticles, produced at high temperature, is generally carried out at the ambient temperature after dilution and/or cooling step. However, this conditioning can lead to a potential structure and size modification of particles. As conventional aerosol metrology equipment is limited to an implementation at ambient temperatures, granular bed filtration could be the system that allows characterization at high temperature without the need of conditioning.

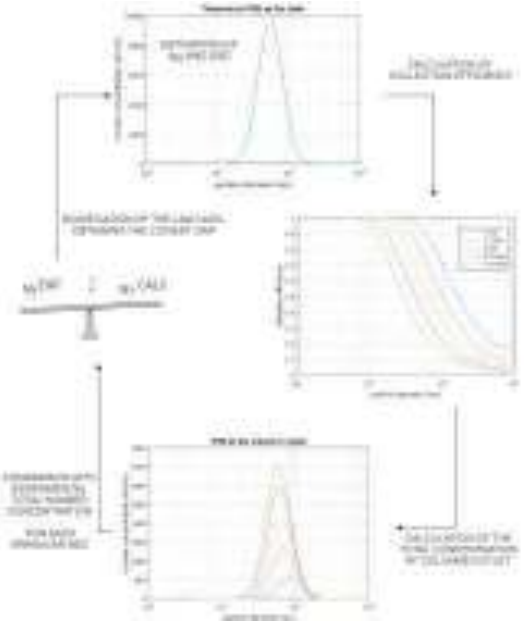
Objectives and stakes

A system of six parallel granular beds, based on previous research [1], adaptable at high temperatures, has been developed to calculate the particle size distribution (PSD). The data inversion calculation allows determining PSD from the total number concentration measured at each granular bed's outlet. At first, tests at ambient temperature are carried out in order to undertake the further research for application at high temperatures.

Methodology / Experimental approach

An inversion data calculation has been developed in order to determine aerosol's particle size distribution, from the six measurements of particle concentration. At first, the calculation of theoretical collection efficiency for each particle size in every granular bed from the known experimental parameters is made. Due to the size of particles (< 100 nm), only the diffusional collection mechanism was taken into account as it is the dominant one. Aerosol's PSD is considered to be lognormal with a random median diameter (d50) and geometric standard deviation (GSD). Knowing the theoretical collection efficiency and this upstream aerosol's PSD, the total number concentration at the outlet of each granular bed is deduced. The deduced values are compared with the experimental values and, by optimization, d50 and GSD are modified until the lowest gap possible between the calculated and experimental total concentrations is obtained.

Illustration: Scheme of data inversion calculation



Main results

The first results with NaCl particles at ambient temperature reveal a good agreement between PSD obtained by data inversion calculation from the six granular beds and PSD simultaneously measured by Scanning Mobility Particle Sizer (SMPS).

The experimental validation for the system of parallel granular beds is in the process for another kind of PSD and another kind of nanoparticles. After this validation at ambient temperature, further research for application at high temperature will follow.

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2018

Electrochemical pressure impedance spectroscopy for transport characterization in electrochemical cells (EPISTEL)

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Keywords: Electrochemistry, Mass Transport phenomena, Proton Exchange Membrane Fuel Cell, Electrochemical Pressure Impedance Spectroscopy, Electrochemical Impedance Spectroscopy, GDL, permeability, Charge Transport

General context

The crucial element for a Proton exchange Membrane Fuel Cell (PEMFC) is its Membrane and its working is governed by various transport phenomena like mass and charge transport.[1] It's important to know the extent of transport phenomena inside the fuel cell, so that we can comment on the efficiency of the fuel cell.[2] There are some conventional techniques, with particularly electrochemical impedance spectroscopy (EIS), transport phenomena are difficult to be distinguished from each other and their signal may be masked by charge-transfer processes.[4] But contrary, electrochemical pressure impedance spectroscopy (EPIS) shows a high sensitivity towards transport processes in fuel cells as shown in illustrated figure. For PEMFC, EPIS is expected to allow the observation of flow and mass transport phenomena with high accuracy.[5]

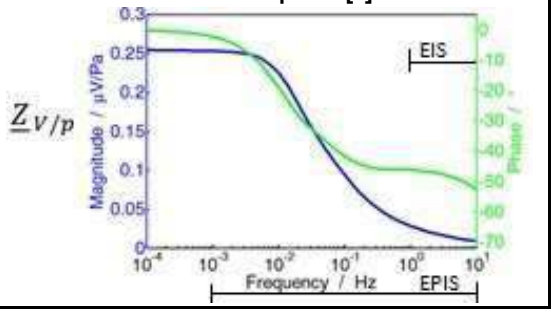
Objectives and stakes

The primary goal of the study is the development and evaluation of EPIS for PEMFC diagnosis in day to day laboratory working. In addition to that, the investigation is expected to bring a significant contribution on understanding, characterization and quantification of the different transport phenomena involving gases and liquid water in the cell. And last but not the least, for cost optimization by using low cost pressure sensor or exciter such as loudspeaker will be tested.

Methodology / Experimental approach

The working of the technique is based on analyzing the dynamic behavior of current/voltage/pressure by either current excitation-pressure detection or pressure excitation-voltage detection with frequency range of 100 Hz to 1 mHz.[1][2] The mass transfer, covering gas transport in the gas diffusion layers (GDL) and the catalyst support also evacuation of the produced water, govern the cell performance.[3] The approach will be progressive, for validation of the EPIS, first we will consider in simple cases, transport phenomena and mass transfer will be observed with dry gases in both the measurement cells and the real fuel cells, before investigating the effect of liquid water in the transport rates in more complex and realistic cases.[2]

Illustration: Simulated EPIS spectra [2]



Expected results:

Since the study is in its very early stage, an experimental bench for the proposed technique is currently being designed. The voltage fluctuation for pressure excitation will be recorded as per the EIS technique used right now. The proposed experimental study will contribute to the further improvement and development of required measurement techniques to analyze electrochemical characteristics, the transport properties.[3]

We expect that the analysis of transport properties in PEMFC within the supply channels, GDL, the microporous layer (MPL) and the catalytic layer, with their influence on the performance of PEMFC with the focus on the water management can be characterized in detail by the suggested measurement tool, the EPIS.

We also expect that EPIS can be used for in situ diagnosis of the fuel cell, e.g. to monitor the nature of the likely causes of any defective behavior in the cell operation. Indication on the state of health of the cell could also be deduced.[5]

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2018

Beneficiation of solids produced by carbonation of olivine for the sequestration of CO_2: separation of nickel by ion exchange

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General context, scientific issues

Chemical processes of carbonation with minerals derived from silicate minerals, e.g. olivine, $Mg_{1,838}Fe_{0,156}Ni_{0,006}(SiO_4)$, have been considered to reduce CO2 emissions. For both economic profitability and environmental acceptance, the recovery of the reaction products has been considered in the global carbonation process.

Objectives and stakes

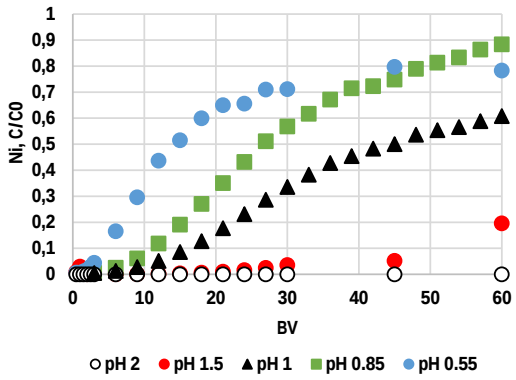
For this purpose, indirect route has been investigated with the sequence of olivine dissolution by reaction with acidic solutions, followed by a series of separation and reaction processes (i) formation and recovery of valuable silica, (ii) separation of Ni^{2+} from the metal salts solution (iii) optimal beneficiation of the Mg, Fe containing solution upon CO_2 carbonation, with recovery of separate fractions.

Methodology/ Experimental approach

In this study focused on steps (ii), ion-exchange (IEX) technique has been selected because of existing technology, reliable resins, and to avoid the use of organic solvents or reactants because of the subsequent pollution of the separated metal solution. Both adsorption and desorption have been considered in the separation process of nickel. Tests have been conducted with the Dowex M4195 resin suitable for removal of nickel from acidic solutions (functional group: bis-picolylamine), in a 150 mm long column, being 15 mm in diameter (21 mL). The model solution contained Ni = 0.025 g/L, Fe = 0.5 g/L, Mg = 2.7 g/L at various concentrations of sulfuric acid: the respective concentrations of metal cations are in accordance with the fluxes to be issued from the olivine dissolution. The solution has been injected using a peristatic pomp, with a flow rate of 3 BV/h. The samples have been collected with an automatic sample changer during the test and analyzed by ICP-OES to evaluate the adsorption kinetics.

Illustration

Selectivity and capacity of the resin for the separation of nickel, depending on the solution pH.



Main results

The results have shown that the adsorption of nickel on the resin depends on the solution pH. The percolation yield of the resin $R_{percolation}$ exceeded 99 % at pH 1.5 and 2, but was only at 40 % at pH 1. Before nickel desorption, the column was rinsed with distilled water (approx. 1.5 BV) to remove sorbed impurities e.g. Mg, Fe. Various conditions have been tested for the elution step. The yield of nickel $R_{elution}$ was approx. 90 % with a purity close to 99 %, using sulfuric acid. However, the nickel enrichment factor (ratio C/C0, i.e. elution concentration/inlet concentration) depends on the acid strength: C/C0 ratios are approx. 35 and 22 using H_2SO_4 1M and H_2SO_4 0,5M respectively. Suitable conditions have been found for both nickel adsorption on the alkaline-based sorbent and production of single Ni solution that confirms the potential of the ion exchange for low concentration of Ni cations. In the global process, the remaining Mg-Fe solution could either been driven to the carbonation stage, or undergo to a second IEX stage for the separation of iron species, but only after oxidation to Fe(III).

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2018

Multiphase flows and interfaicial phenomena at different scales

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Axe PErSeVAL | SysPol

Keywords: Magnetic control, ferrofluid, interfacial dynamics, droplet formation

General context, scientific issues

Accurate and effective control of the droplet size has great potential and extensive application prospect in the fields of chemical analysis, medicine, biology and materials synthesis[1]. Magnetic modulation provides a new wireless approach for the control of ferrofluid droplets[2]. To the best of our knowledge, the understanding on the interfacial dynamics of ferrofluid droplet formation in a T-junction remains still far from sufficient up to date[3-4], and the scaling law of ferrofluid droplet size under the magnetic field is also lacking.

Objectives and stakes

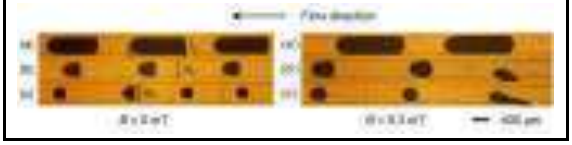
The present study aims to investigate the effects of two-phase flow rates and magnetic flux density on the flow regime, interfacial dynamics of ferrofluid droplet formation and droplet size, expecting to provide the basis for the precise manipulation of ferrofluid droplets by magnetic forces and open new windows for the widespread application of the magnetic micro-emulsions in the fields such as biological, medicine and precision instrument control.

Methodology / Experimental approach

Water-based ferrofluid was employed as the dispersed phase. Mineral oil with 4 wt% surfactant sorbitan laurate (Span 20) was used as the continuous phase. The two-phase fluids were injected into the T-junction by two syringe pumps. The ranges of the volumetric flow rates of the two-phase fluids were $0.5 < Q_d < 1.5$ mL·h^{-1} and $0.25 < Q_c < 30$ mL·h^{-1}, respectively.

A high-speed camera coupled with a microscope was used to record the droplet formation process. The system was supplied with sufficient illumination by a halogen lamp placing at the other side of the microfluidic device. The non-uniform magnetic field was realized by a neodymium iron boron (NdFeB) magnet. The magnetic flux density at the T-junction was altered by adjusting the separation distance between the permanent magnet and the T-junction. The magnetic flux density was measured by a Gauss meter and increases with decreasing the distance.

Illustration: Micrographs of different flow regimes of the ferrofluid droplets in a T-junction.



Main results

In this study, the magnetic modulation of the non-uniform external magnetic field on the interfacial dynamics of ferrofluid droplet formation in the T-junction was investigated. The slug flow, slug-dripping transition flow and dripping flow were observed. The transition from the slug-dripping transition flow to the slug flow was promoted by increasing the magnetic flux density. The presence of the magnetic field increased the radius of curvature of the droplet neck, prolonged the droplet generation cycle and decreased the frequency of ferrofluid droplet formation. It was found that the increasing rate of the length for the thread tip l_t and the expanding rate of the dispersed neck decreased with the magnetic flux density. The magnetic flux density had a remarkable effect on the increasing rate of l_t during the squeezing and pinch-off stage. The maximum of w_m is positively correlated to the magnetic flux density and the moment at which the appearance of the maximum is delayed with increasing the magnetic flux density. A modified scaling law for the ferrofluid droplet size was proposed in two ranges by taking the two-phase flow rate ratio, capillary number and magnetic Bond number into account.

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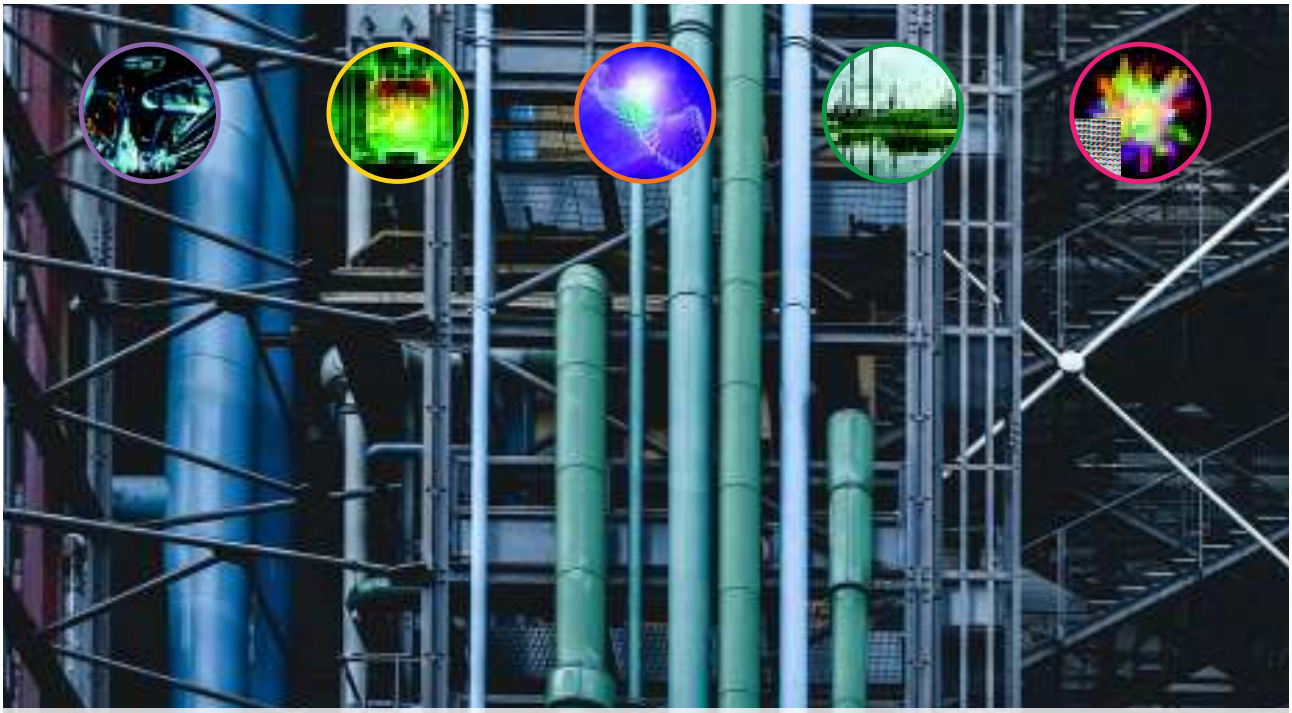


PRIMO

PROCESSES, REACTORS, INTENSIFICATION, MEMBRANES, OPTIMIZATION

LRGP
LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

2018	Optimal shape design of Hollow membrane modules **Omran ABUSHAMMALA (1st year)** **Eric FAVRE, Rainier HREIZ** **Axe PRIMO I EMSP**	

Keywords: CFD, Numerical simulation, Membrane separation, Dean Vortices, Mass transfer, Optimization.

General context, scientific issues

Membrane separation is widely used for the separation of homogeneous liquid or gaseous mixtures, and is one of the most promising intensification technologies for gas-liquid absorption processes [1]. The design and operation of membrane modules have been of great interest for many scientific researches aiming at improving the separation efficiency. In this context, CFD (computational fluid dynamics) reveals to be a powerful tool for assisting and supporting engineers for determining the optimal shape of membrane modules. This Ph.D. consists in a CFD study of the performance of helical shape hollow membranes.

Objectives and stakes

The goal is to determine the effects of the helix geometry (pitch, helical radius and pipe diameter) on:

• The achieved mass transfer efficiency (generally expressed by the Sherwood number).

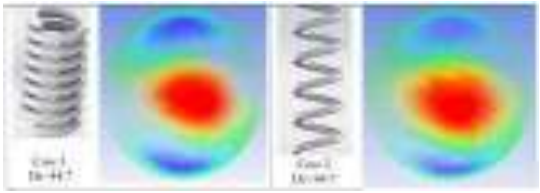
• The involved pressure drop (generally characterized via a friction factor) as pumping constitutes a major operating cost.

• The packing density or compactness which represents the highest membrane surface that can be packed within a unit volume.

Methodology / Experimental approach

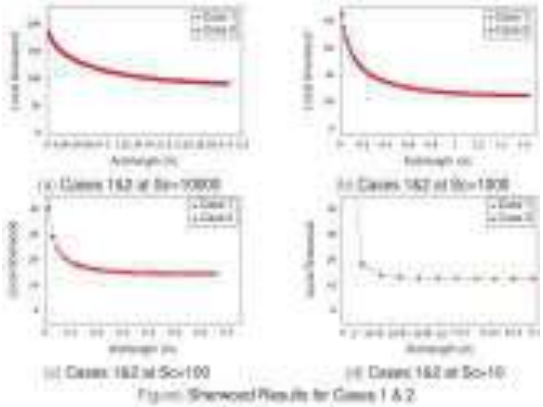
The performance of different membrane designs will be investigated via CFD simulations. Several geometries will be considered such as designs that induce secondary flows, geometries leading to chaotic mixing effects, as well as the use of obstacles for promoting local turbulence or inducing swirl effects. The optimal dimensions for each of these designs will be determined using an optimization algorithm. Several optimization criteria will be considered (i.e. multi-objective optimization): the mass transfer efficiency, the pressure drop, and the compactness, etc. Designs leading to the most significant improvements of these objectives will be fabricated by additive manufacturing so as to allow an experimental confirmation of the numerical results.

Illustration: Velocity profiles (Dean Vortices) at Outlet Plane for Case 1& 2 at Re=100. Which Case 1 to helical membrane shape with helical radius R=2.5mm and helical pitch P=1.25mm as case 2 has the same helical radius with case 1 that a triple pitch P=3.75mm.



Main results

The cases have studied for different Schmidt numbers at Sc=10,100,1000,10000 and Re=400. The results obtained from the two cases were similar with a slight improvement has case 2. This is due to the torsion factor which is larger for Case 1 than Case 2.



- The Sherwood number increases when the Reynolds number increases, and it is affected by helical coil diameter much more than by the helical pitch.
- For large Schmidt numbers, the Sherwood number significantly decreases when torsion increases. However, for small Schmidt numbers, the Sherwood number declined slightly as the torsion increased [2].

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2018

Compact heat exchanger reactor modelling

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Keywords: Heat exchanger-reactor, plate-fin heat exchanger, process simulation, reaction, catalyst, reactive fin efficiencies, microchannel.

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 [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. A simplified 1D version of the tool will be developed and validated with experimental and CFD simulation results. The CFD simulation should also allow understanding the physical phenomena occurring in the heat exchanger reactor.

Methodology / Experimental approach

The 1D program which is currently under development includes homogeneous and heterogeneous models (featuring external heat and mass transfer considerations) that enable the simulation of simultaneous catalytic and fluid phase chemical reaction in a heat exchanger. Plate-fin heat exchanger was chosen as general frame for the simulation tool.

The CFD simulation of both a reactive flow in a channel and a set of several channels are done to understand the physical phenomena occurring at local and global scales respectively (i.e. external and internal mass transfer, coupling between heat and mass transfer, conduction, non-uniform distribution in the channels, ...). These simulations investigate the impact of major assumptions that were made to simplify the model, such as heat conduction effects in a section of the metal frame, perpendicular to the flow.

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

Main results

Several heat transfer phenomena occur in plates and fins heat exchangers, such as convection and conduction. The competition between both is responsible for non-negligible temperature gradients in fins [4]. In the specific case of reactive plates and fins heat exchangers, by absorbing or releasing heat at the fin surface, the catalytic reaction affects significantly the fin and by-pass efficiencies. As a consequence, the classical expressions available in the literature for these efficiencies are no longer correct. Not taking into account these differences would lead to overestimating both heat transfer and kinetics, the last one being critical because the kinetics depend exponentially on the temperature.

A new simplified fin model was developed at channel scale in order to estimate heat transfer, reaction and by-pass efficiencies for a reactive fin. Even if restrictive assumptions had to be made, this model shows very good agreement with a real fin subjected to a real flow simulated in Fluent.

At exchanger scale, the competition between conduction, convection and heat absorption was investigated and showed very little impact on the Air Liquide heat exchanger reactor performances.

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2018

Dynamic real-time optimization of a graft polymerization process

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Axe PRIMO | ODCA

Keywords: Graft polymerization process, dynamic optimization, moving horizon state observer, experimental implementation.

General context, scientific issues

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

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

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

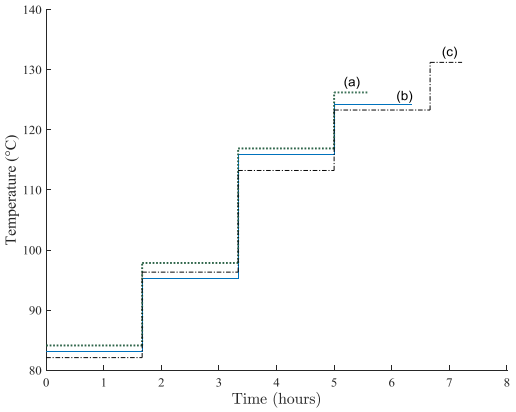
Objectives and stakes

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

Methodology / Experimental approach

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

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



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

Main results

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

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2018

Optimization of Architecture of Membrane Process

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Keywords: Membrane gas separation, Process optimization, process system engineering, Global optimization, Non-linear optimization.

General context, scientific issues

Membrane gas separation by means of synthetic polymeric membranes is a well-established technology for several industrial applications [1]. However, because of the inherent limitations of the solution-diffusion separation in polymeric membranes, several separation stages are often necessary when applications demand high levels of performances, and/or when the feed is poor in the component(s) to be recovered. Therefore, the development of an accurate and reliable process strategy is essential in order to optimize the performances and the global costs of such processes.

Objectives and stakes

The objective of this thesis is to develop and apply an optimization methodology in order to design the optimal structure of membrane separation processes that maximizes operation performances (recovery and purity) and minimizes costs (CAPEX, OPEX) of the system.

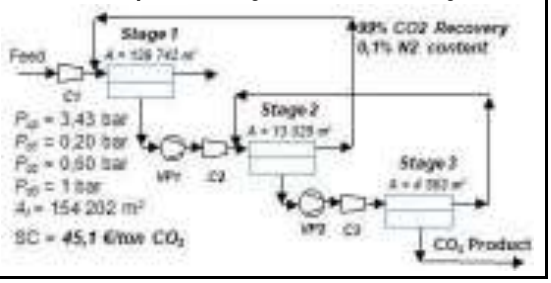
Methodology / Experimental approach

This work presents the development and application of a Non-linear Programming (NLP) approach based on a superstructure for the design and optimization of multistage membrane separation processes. The optimization is based on a Non-linear global optimization strategy [2]. This strategy allows the exploration of a wide area of the feasible region during the global search phase. Also, it allows the intensification of the search for the potential better solutions near the local optima through the local search phase. Thus it improves the chances of finding optimal process configurations.

In the first step, the approach was validated by comparing its output with that of a reference work from the literature [3], dealing with the optimization of multistage membrane processes for natural gas treatment.

After validation of the optimization approach, it has been applied to the recovery of CO_2 from Blast Furnace Gas (BFG). The effect of CO_2 recovery and residual N_2 constraints on optimal process configuration, operation variables (upstream and downstream pressures and membrane surface) and separation cost is studied for varying purity and recovery constraints, i.e. 90- 99% CO_2 and 1- 0.1 % N_2 content. Process configurations from 2 to 4 membrane stages have been considered.

Illustration: Optimal 3-stages membrane configuration



Main results

Regarding the comparison of our results with the reference cases from the literature [3], a significant decrease of the objective value has been found. This validation allows us to be confident of the effectiveness of the method.

In addition, concerning the recovery of CO_2 from BFG, very detailed analysis has been performed. The CO_2 separation cost was in the range of 29 to 75.7 EUR/tonCO_2 for the two-stage processes. As a matter of fact, the separation cost increases quickly for the two-stage configurations by increasing of purity and recovery constraints. The use of three-stage configurations allows to reduce separation cost when high recovery and/or purity is required. Separation costs in the range of 29 to 45.1 EUR/tonCO_2 were calculated in this case. Furthermore, no remarkable improvements in separation costs were obtained for process configurations with four membrane stages. Small reductions of less than 1EUR/tonCO_2 in some cases are not considered to be relevant enough to justify the increasing complexity when considering real-life operation.

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2018

Modeling and analysis of the behavior of the air purification boxes used in construction machinery for the protection of operators against gases and vapors

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Keywords: gas and vapor treatment boxes, adsorption with chemical reaction of ammonia, experimental analysis, modeling, simulation, optimization

General context/scientific issues

The air purification boxes considered here are used in the pressurized clean air cabins (PCAC). They consist of two separation parts in series: a filter that allows the separation of solid particles and / or aerosols and a bed of activated carbon that allows the elimination of toxic or harmful gases by adsorption [1]. Although some research contributions are devoted to the study of the effectiveness of the PCACs with regard to particle protection, the gas and vapor treatment boxes have not been extensively investigated and very few scientific and technical studies are available in the open literature.

Objectives and stakes

The main goal of this work is to develop both scientific and technical knowledge on the operation of adsorbent boxes equipping the pressurized clean air cabins (PCAC). More specifically, the objectives are:
(i) to optimize the design and sizing of these boxes and to control their operation.
(ii) to better simulate the influence of operating cycles
(iii) to improve the existing boxes in order to increase their life duration.

Methodology / Experimental approach

We propose to carry out an experimental study and develop a fine and accurate first principle model taking into account all the phenomena involved and based on the following equations:

Material balance equations [2]:

$$\frac{\partial c_i}{\partial t} + u\nabla c_i + \nabla(-D_L \nabla c_i) = r_{x,i} \qquad (1)$$

Chemical reaction rate [3]:

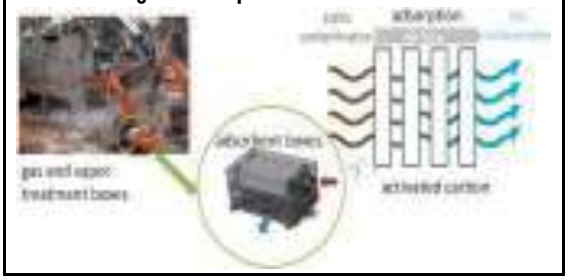
$$r_{x,i} = -\frac{(1-\varepsilon)}{\varepsilon}\rho_s \frac{\partial q_i}{\partial t} - k_c \frac{bc}{1+bc}\left(1-\frac{q_i}{q_m}\right)^2 \qquad (2)$$

Kinetics of adsorption relation [4]:

$$\frac{\partial q_i}{\partial t} = k_{LDF}(q_e - q_i) \qquad (3)$$

Once identified and validated by the experiment, the resulting model will be exploited to optimize the design and operation of these adsorbent boxes.

Illustration: gas and vapor treatment boxes



Expected results

-Characterization of activated carbon and impregnated activated carbon with zinc sulfate (BET, MEB, porosity, density).
-Measurements of adsorption isotherms of ammonia, water and binary ammonia-water on (impregnated or not) activated carbon.
-Development of global estimability analysis to rank the unknown parameters involved in the model [5] and eventually designs optimal experiments In order to accurately determine the most influencing parameters.
-Optimization of the design, sizing and operation of the adsorbent boxes.

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2018

Intensification of a catalytic reactor for the production of acrolein

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Keywords: Heat exchanger-reactor, kinetic modelling, process simulation, catalyst, CFD

General context, scientific issues

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

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

Objectives and stakes

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

Methodology / Experimental approach

In order to design a new reactor, the kinetics of the several reactions occurring in the reactor have to be clearly determined.

A kinetic model, based on Redlingshofer et al. work [2], has been developed, with numerous kinetics parameters that have been estimated using experimental data provided by a team of the UCCS.

This new kinetic model was then used to design an intensified heat exchanger reactor, using a constraint map methodology representing different performance criteria (yield, conversion, hot spot temperature) as a function of channel numbers and cooling temperature [3].

The design of the intensified reactor was then validated by CFD simulation. Velocity profiles enable to validate the flow distribution as temperature profiles allow to study heat transfer. These profiles were exploited to estimate mechanical stress of the metallic structure.

A pilot unit will be created by additive manufacturing by the factory Poly-Shape, which is part of the project.

Illustration: Constraint map for a range of cooling temperature and number of reactive channels in the intensified reactor

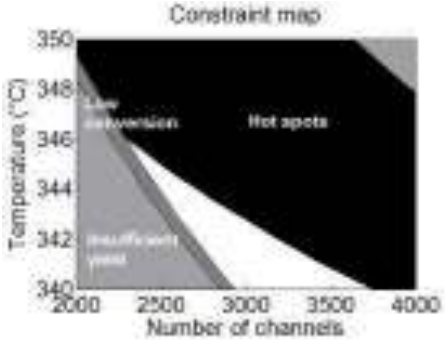
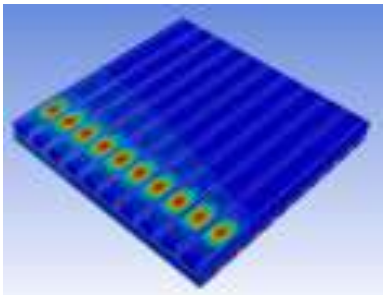


Illustration: Temperature map for hot spot formation due to exothermal reactions in reactive channels



Main results

- Identification of parameters for the kinetic model
- Preliminary sizing of the intensified reactor
- Validation of the design by CFD simulations (ANSYS Fluent).

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2018	Optimal design of fixed bed reactors using additive manufacturing Alexis COURTAIS (1st year) François LESAGE, Abderrazak.LATIFI Axe PRIMO | ODCA	

Keywords: Shape optimization, Fixed bed, Additive Manufacturing, Computational Fluid Dynamics (CFD), OpenFOAM, Adjoint Problem

General context/scientific issues

To improve its competitiveness, the chemical industry must constantly innovate and evolve towards more intensified, efficient and compact processes. The shape of the units that make up the process represents a fundamental scientific, technical and technological challenge. Shape optimization is a technology that is quite appropriate to meet this challenge. It consists of a set of mathematical methods that allow to find the best shape of an object which minimizes a cost function while satisfying given constraints. Originally, shape optimization in the context of fluid dynamics has been developed for aerodynamic industry and particularly for aircrafts. More recently, it has been used in chemical engineering to determine the optimal shape of a pipe for example [1].

Objectives and stakes

The aim of the thesis is to design and manufacture topologically optimized fixed bed contactors. The optimization consists in moving, creating or removing the contactor inner or external boundaries. It relies on the shape derivative concept, and does not require any parametrization of the involved geometries. However, the optimal shape is subject to manufacturing constraints. The resulting optimal shape of the contactor will be manufactured using additive manufacturing technology and a campaign of experiences will be carried out to validate the simulation.

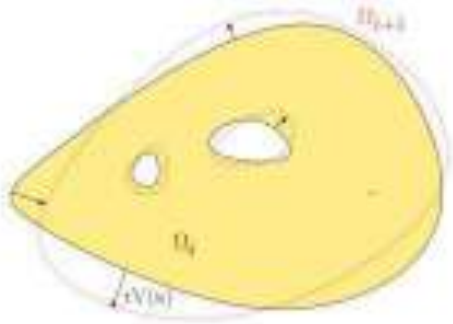
Methodology / Experimental approach

Before tackling the fixed-bed 3D contactor, a first goal of the thesis was to find the optimal shape of an obstacle to a 2D flow. In this case, the constraint chosen is an iso-volume constraint and the optimization criterion is the energy lost by the fluid due to the viscous friction.

The solution of the Navier-Stokes equations in (U,p) and of the adjoint problem (U_a,p_a) will allow to compute the displacement vector V(x) which will define the border of the new iteration's domain (like on the illustration) [2].

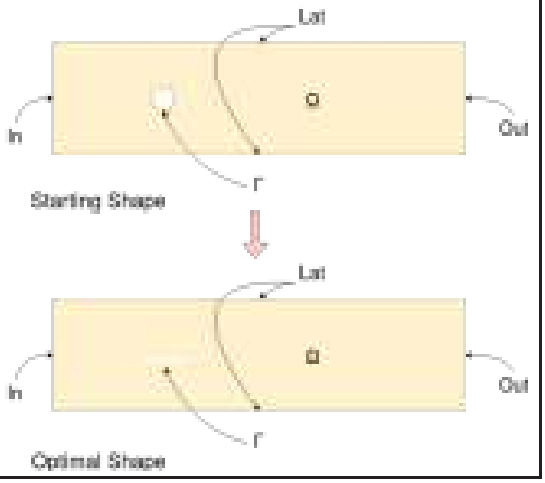
OpenFOAM is an open access CFD software. A solver of this software has been modified to code the algorithm which find the best shape of the obstacle.

Illustration: Example of an iteration of the shape optimization's method



Main results

Starting from a circular obstacle and where the only border which can move is Γ, the optimal shape can be obtained and it seems to be a very flattened oval. This result was expected because this kind of optimal shape minimizes the disturbance of the flow.



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2018

Design and optimization of a distributed energy system with hydrogen like energy vector

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Axe PRIMO | PRISM

Keywords: Hydrogen, distributed energy system, renewable energies, optimization, decarbonization, power-to-gas, eco-district.

General context, scientific issues

The emergence of distributed energy systems (DES) and the growing share of renewable energies are changing the way in which power systems are planned, designed and operated [1]. DES are based on the idea to replace or complement the big and conventional centralized generation plants, with smaller units located close to energy consumers[2]. In addition to offering more flexibility in generation, reducing inefficiencies in delivering and vulnerability of the system, DES enable to take advantage of the synergies among different sources and energy carriers. It provides a reliable pathway for energy transition from technological, economic, environmental and social point of view.

Among energy carriers, hydrogen has emerged as a friendly solution for climate change, air pollution and energy security. Hydrogen has a wide range of properties to be used as fuel, raw material or as interface between electricity and chemical energy forms through the power-to-gas process. Its great content of energy per mass, that is around of three times bigger than common fossil-derived fuels, and its capability to enable the decarbonization of some chemical processes and transport sector, made hydrogen a key energy carrier to face the current energy and environmental challenges [3,4].

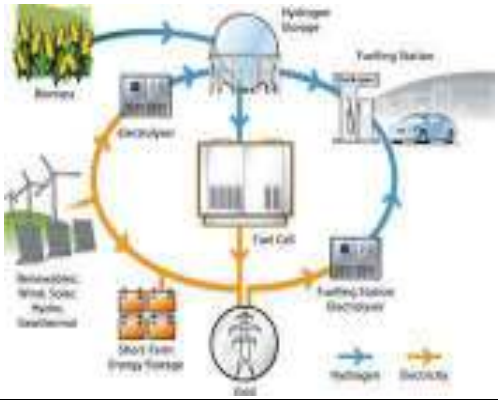
Objectives and stakes

Design and optimize an energy system for an eco-district by using hydrogen like energy vector

Methodology / Experimental approach

Introducing hydrogen into DES is a complex problem, and as a consequence, an integrated approach including several aspects is required. From the technical point of view, a set of potential technological alternatives must be evaluated in order to establish their complementarities and build the most adequate configuration. Moreover, this set of possible configurations, under economic, environmental and socio/political dimensions also need to be studied, and fitted to conditions (climate, resources availability) of the specific context where it would be implemented.

Illustration: Hydrogen-based energy system



Expected results

The main expected result of the project is the basis to propose a methodological approach to design context-adapted DES under sustainability dimensions.

These results include the optimal design of equipment running in stationary and transient regimes and the best transient regimes of multi-energy supply. On the other hand, considering the variability of energy usages and sources, an important result is also to propose criteria for the size of district as a function of its social and economic activities.

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2018

Experimental characterization and design of a millichannel vaporiser

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Keywords: Milli-channel, Vaporiser, Sizing, Design, Experimental study

General context, scientific issues

Hydrogen is probably the fuel of the future. There is an ever-growing interest on its production and its new applications. Some of these require an on-site production; the storage of H_2 is a well-known issue.

One of the goals of the FAIR project is to design an intensified SMR (Steam methane reformer).

Two elements of the SMR are intensified: the heat-exchanger reactor and the vaporiser. The vaporiser will be designed to valorise waste heat provided by hot fumes leaving the heat-exchanger reactor.

Objectives and stakes

The objective of this project is to design a milli-channel vaporiser providing the high-pressure steam required by the chemical reaction.

Two different vaporisers will be designed: the first one will enable to understand hydrodynamics and heat-exchange that govern boiling in milli-channels at "low pressures" (1-5 bars); the second one will be the characterisation of a pilot-scale vaporiser made by additive manufacturing supporting "high pressures" (16-25 bars).

Methodology / Experimental approach

The main issue of the study of vaporization is to determine the vapour quality. It has been chosen that it will be calculated by heat balance on the Low-Pressure Vaporizer (LPV).

To assess properly this quality, a first campaign is performed to characterize the heat losses of the vaporizer. The flowrate and the temperature of the oil are changed in order to cover the various operating conditions.

In a second time, a new campaign will be done to understand the phenomena of the vaporization in milli-channels. The wall temperatures, the temperature of and the flowrate of both fluids are considered. An additional study is performed using a high frequency camera in order to highlight the nucleation and the growth of bubbles in the channels.

Illustration: Test bench built

Main results

The first experiments performed with the test bench proved that a certain flowrate of water could be totally vaporized in the LPV. Obviously, the goal of 2 L/h as the final flowrate vaporized by the LPV is not reached yet.

The analysis of the data given by the high frequency camera shows that the channels are not independent. There exists a communication of water between all channels because of the non-flatness of the window of visualization. However, despite this fact, the growth of a bubble in a channel was observed, as well as the effect of overpressure that pushes the liquid forward and backward in the channels.

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2018

Computer-aided model development for liquid-phase synthesis systems

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Axe PRIMO | PRISM

Keywords: Model development, Model superstructure, Computer-aided software, Ethanolysis

General context, scientific issues

Accurate models describing quantitatively the behavior of chemical syntheses are essential for the optimization of reactor performances.

Objectives and stakes

The objective of this work is to develop a methodology for systematic model development for liquid-phase syntheses and a computer-aided software, facilitating the user's work. To demonstrate the feasibility of the methodology and the practicability of the software, the NaOH-catalyzed ethanolysis of sunflower oil has been selected.

Methodology / Experimental approach

The methodology (illustrated in Figure 1) consists of an external loop for model structure development, i.e. identification of the reactions in the synthesis system, and an internal loop for model parameter development, i.e. identification of the parameters with an acceptable precision for the chosen model structure.

The model superstructure is defined as the set of all feasible chemical and physical reactions between all possible species in the synthesis system. The mass transfers are considered as physical reactions, in which the species transfer from one phase to another phase. Any model structure is a subset extracted from the model superstructure.

Several reactors are incorporated in the methodology, which enlarges the experimental window and thus enhances the efficiency of model parameter precision and accelerates the reactor performance improvement. The methodology allows identifying simultaneously an accurate model fitting all experiments comprising the preliminary experiments, the data acquisition experiments and the validation experiments, as well as the optimal reactor and its associated optimal operating conditions for the given synthesis.

In order to make the model development easier and faster, a computer-aided software is developed using MATLAB R2014a. It guides the user through the steps of the workflow (illustrated in Figure 2).

Illustration:

Figure1: Systematic procedure for model development

Figure2: Software workflow

Main results

The methodology has been successfully applied to identify an appropriate model (structure and parameters) for the NaOH-catalyzed ethanolysis of sunflower oil system. Furthermore, the generality of the methodology will be validated by more liquid-phase synthesis systems.

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2018

Organic Aerogels based on natural amino acids : Super Thermal Insulators

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Axe PRIMO | EMSP

Keywords: Aerogels, organogels, monolith, composite, mass transfer, Computational fluid dynamics (CFD), Ansys-Fluent, thermodynamics, ASPEN

General context, scientific issues

The use of highly insulating material can lead to a significant decrease of energy consumption. This is why the researchers focused on super-insulating materials possessing a thermal conductivity lower than that of the air, 25 $mW.m^{-1}.K$, such as aerogels [1].

Objectives and stakes

As part of the ADEME project AEROSITAN, the objective of this post-doc is to study the aerogel production through supercritical drying of organogels. We focus in particular on the optimization of the process in order to apply it to 100 x 100 x 10 mm^3 samples and then to extrapolate it to an industrial scale.

Methodology / Experimental approach

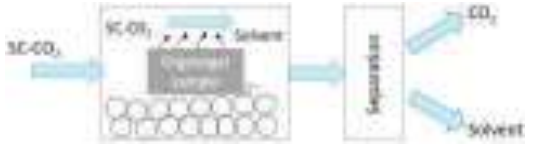
The process of CO_2 supercritical drying of both monolithic and composite organogels is first studied experimentally. It consists in three steps: supercritical CO_2 (SC-CO_2) preparation, organogel drying in an autoclave and CO_2-solvent separation. During drying, a parallelepiped organogel sample (45 x 45 x 5 mm3) is swept by supercritical CO_2 in which the solvent (3-penthanol) contained in the organogel, dissolves and is driven to the exit of the autoclave [2]. We are interested in the material balance of the solvent, which should be completely recovered. The experimental solvent recovery for different CO_2 flow rates is calculated. From the experiments the drying kinetics is also obtained.

Numerous experiments are conducted in order to determine the optimal conditions for the supercritical drying.

A thermodynamic study is then carried out to model the cyclonic separation of the CO_2-solvent mixture with Aspen Plus software [3].

Furthermore, the drying in the autoclave is simulated with CFD software ANSYS-fluent, considering the solvent transfer from the gel into the CO_2 stream by diffusion and convection

Illustration: Simplified diagram of the drying process of an organogel by supercritical CO_2 (SC-CO_2)



Main results

The theoretical results obtained by the thermodynamic modeling are compared to experimental recovery rate. For the moment, the model does not represent correctly the experimental data.

It is noteworthy that the theoretical optimal conditions for the cyclonic separation are closed to the experimental conditions.

The drying step in the autoclave is also modelled and both the organogel sample and the surrounding fluid in the autoclave volume are simulated with CFD (Computational fluid dynamics) using ANSYS-Fluent software. The developed model takes into account not only the thermodynamic data of the considered system, but also mass transfer mechanisms, based on Fick's law. The diffusion coefficient of 3-pentanol in CO_2 is calculated using Stokes-Einstein theory.

The obtained theoretical drying kinetics for the monolith organogel are compared to the experimental curves. The theoretical kinetics is found faster than the experimental kinetics.

Both monolithic and composite gels have been dried experimentally. But so far, only monolithic gels have been simulated. The theoretical kinetics for composite gel will be determined in the future, in order to validate the proposed model, determine the mass transfer parameters and then size the industrial process for both organogels types, monolith and composite.

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2018

Pushing the intensification of membrane module systems: materials vs process potentialities.

Deisy MEJIA (3st year)

Eric FAVRE, Cecile LEMAITRE, Christophe CASTEL
AXE PRIMO | EMSP

General context, scientific issues

Membrane are present in most industrial sectors and are used in large and very diverse amount of applications. Even though, not all membrane technologies are developed industrially and there is a need for optimized membrane modules.

Processes intensification is important for the development of the new industry and is a way to advance through more environmentally friendly and efficient practices and membrane processes are part of the change to achieve these objectives.

Objectives and stakes:

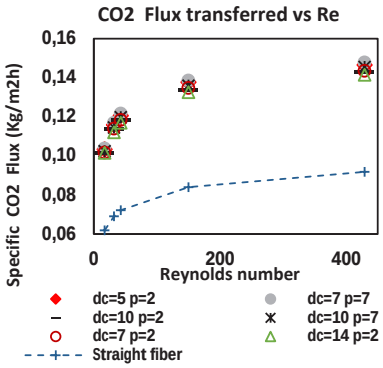
Three membrane technologies were chosen for this study: gas-liquid contactors, membranes distillation and reverse osmosis. The main objectives were:

1. To identify the main disadvantages in the membrane technologies studied.
2. To propose solutions to overcome the issues related to membrane wetting (dense membrane), concentration and temperature polarization (Dean vortices).
3. Evaluate the solutions proposed to define which methodology is the most adapted.
4. Analyze the interconnection of the variables studied, and how they affect the module efficiency.

Methodology/ Experimental approach

Process simulation was the main tool implemented in order to study and to analyze each process. A one dimensional model was developed in Matlab for Gas liquid contactors, membrane distillation and reverse osmosis. The models were compared to experiments and data from literature in order to be validated. CFD simulation was used to evaluate Dean vortices and the impact of curved geometries on heat and mass transfer coefficients. The apparition of Dean vortices were visualized using RMI technique and velocity profiles were validated as well.

Illustration Flux increment using helical fibers



Main results

- It has been demonstrated that not real advances can be done if both domains: materials and processes are not developed at the same time.
- Increasing indefinitely the membrane permeance does not necessarily implies a higher flux and efficiency.
- Mass transfer is increased in 50% to 70% when using helical fiber arrangements in gas liquid contactors, 20% in membrane distillation and for reverse osmosis, the vessel volume can be reduce.

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2018

Surface modification of commercial membranes for Organic Solvent Nanofiltration (OSN)

Mahbub MORSHED

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Axe PRIMO | EMSP

Keywords: Organic solvent nanofiltration (OSN), commerical OSN membranes, surface treatment, transport mechanism.

General context, scientific issues

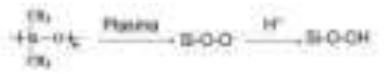
Conventional separation processes in chemical industries are energy intensive and acounts for 40-70% of the total production cost. OSN can be a good alternative for a cost effective and environment friendly technology to replace conventional separation processes such as distilliation, liquid-liquid extraction etc. A good example is Max-Dewax process for lube oil purification, where OSN is commercially applied and successful.

Objective

The main objective is to modify commercial OSN membranes in order to fine tune surface properties to obtain better separation characteristics. Cross flow nanofiltration with pure and/or mixture of solvent, solvent-solute binary and/or multicomponent systems have been studied, characterized and optimized ; in terms of flux and retention behaviour. Finally, the knowledge obtained will be applied to recover and reuse homogeneous catalyst in organic media.

Methodology / Experimental approach

Step 1 : Post discharge plasma creates active molecular species which are able to functionalize PDMS membrane surface.

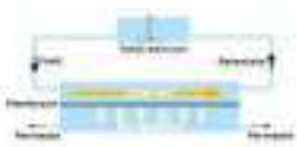


Scheme 1: Plasma modification of PDMS based membrane.

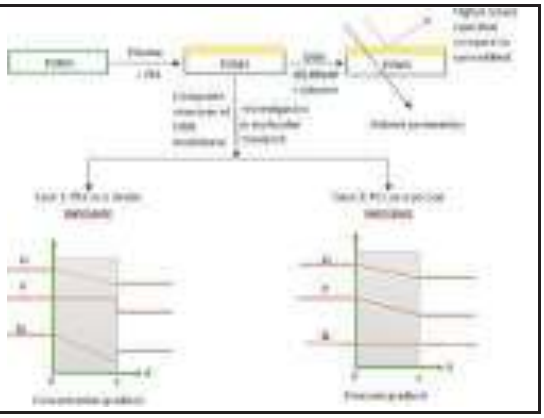
Step 2 : Polyelectrolyte multilayer (PEL) by layer by layer (LbL) onto the functionalized surface.

Scheme2 : LbL coater robot

Step 3 : Cross flow OSN of pristine, plasma &PE modified membranes.



Scheme3 : OSN and laboratory set-up for experiemnt.



Main results

- Plasma exposure time was optimized and found that only 30 s exposure of Ar/O_2 plasma effectively convert PDMS surface from hydrophobic (water contact angle 103 °) to hydrophilic (30 °).
- Retention of a model solute, RBINAP (organometalic ligand) in PDMS was obtained as 80% and retention of ToABr, a phase transfer catalyst (ToABr) was obtained 93% which indicates the potentiality of PDMS membrane in catalyst and ligand recovery.
- After plasma, polyelectrolyte modified PDMS samples were prepared as indicated in methodology and tested with OSN in 10-40 bars of TMP. RBINAP rejection in modified membrane was obtained 88% with 10 PEL-bilayers and 95% with 20 bilayers. Solvent (toluene) flux decreased in both cases. ToABr rejection improved to 97% in PEL modified membrane.
- Apart from catalyst and ligand, linear alkane from C16 to C44 have been tested as well as ternary mixture of RBINAP and C16 in toluene. In each cases, modified membrane gives an improved rejection compare to the pristine memebrane. Retention in ternary mixture gives similar result as binaries. Thus couplinng effect is not evident in these systems .

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2018

Study and development of hybrid processes integrating membrane technologies for purification of bio-based molecules

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Keywords: Pervaporation, vapor permeation, membrane contactor, hybrid processes, sustainable development, bio-based molecules, purification processes, energy efficiency, simulation, modelling

General context, scientific issues

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

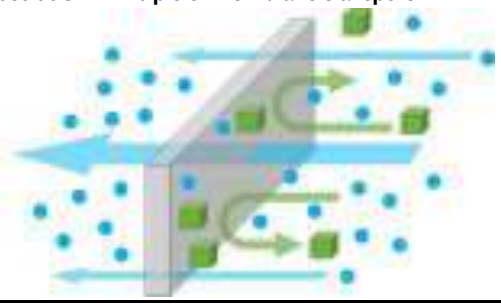
Objectives and stakes

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

Methodology / Experimental approach

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

Illustration: Principle of membrane transport



Main results

Confidential

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2018

Modeling, simulation, dynamic optimization and nonlinear control of a reactive evaporation process for synthesis and deposition of zinc oxide thin films

Asdrubal RAMIREZ (1st year)

Gerardo GUZMAN , Abderrazak LATIFI
Axe PRIMO | ODCA

Keywords: Plasma Assisted Reactive Evaporation (PARE), State estimation, Dynamic optimization, Non-linear control

General context, scientific issues

Zinc oxide (ZnO) is a semiconductor material characterized by having many interesting optoelectronic properties such as a wideband gap, a large exciting binding energy of 60 meV and high transparency in the visible region, which has made way for many applications, including flat panel display, light emitting diodes, and solar cells [1-2]. The demand for ZnO thin films has increased in an exponential way in the last 20 years. Various methods, such as RF magnetron sputtering, reactive sputtering, CVD, CBD, spray pyrolysis and sol gel techniques have been used to fabricate ZnO films. Among these methods, magnetron RF-sputtering is considered the most favorable technique for large area deposition and mass production. However, the RF-sputtering deposition process has cost limitations in large-area manufacturing, associated with the use of ceramic targets. In contrast, ZnO deposited by Plasma Assisted Reactive Evaporation (PARE) with Zn as the starting material is in terms of cost and large-scale production better than the RF-sputtering method. Additionally this system allow deposition of thin films of both, i-ZnO and n+-ZnO films due the possibility of change the O_2 density vacancies.

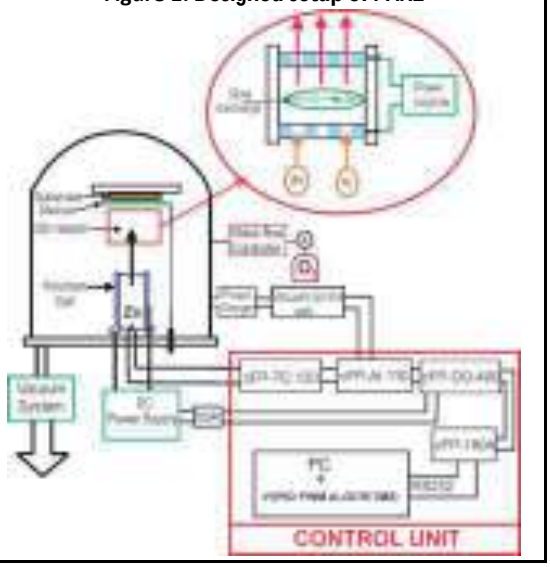
Objectives and stakes

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

Methodology / Experimental approach

The approach adopted here consists of:
1. Build a dynamic model for a pilot PARE reactor to represent the operating system and to predict the main state variables configuration.
2. Calculate by means of dynamic optimization the optimal time profiles (flow rates, pressure and temperature) required in the PARE system to maximize the ZnO thin film production or minimize the batch time, subject to constraints on the final product quality and reactor.
3. Implement state estimators or observers of the state variables such as an extended Kalman filter to be used in the application of a state-space control technique and provide valuable information for monitoring.
4. Develop and implement a nonlinear geometric control strategy using virtual instruments for a pilot reactive evaporation reactor. The selected dynamic state space model will serve to obtain an optimal trajectory, develop the control law, estimate the states and will be used to test the final performance.

Figure 1: Designed setup of PARE



Main results

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

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2018

Membrane separation processes for steelmaking gases treatment: optimal design for carbon capture and hydrogen recovery

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Eric FAVRE, Christophe CASTEL

Axe PRIMO | EMSP

Keywords: Gas separation, polymer membrane, blast furnace gas (BFG), dense membrane, carbon capture and utilization.

General context, scientific issues

The Iron and steel sector is the second largest industrial energy user and the largest industrial source of CO2 emissions. New research programs are considering a carbon capture and utilization perspective with the objective of valorizing available residuary gases during steel manufacturing considering commercial gas separation membranes available today Ramirez-Santos et al. (2016). One of main issues that play a key role when considering the economic feasibility of the overall process is the design of an optimized multi-stage separation architecture depending on the purity-recovery constraints imposed on the separated species (CO_2, H_2) by the utilization alternative under consideration (EOR, chemical transformations, biological transformations). This work addresses the development of a process design methodology by means of a superstructure-based optimization and its application to commercially available gas separation membranes for CO_2 and H_2 recovery from BFG and COG.

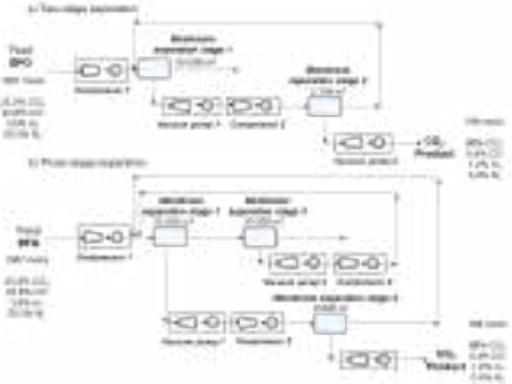
Objectives and stakes

This work follows the results of a thesis (2017) 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%.

Methodology / Experimental approach

A monotonic basin hopping algorithm was used to solve the optimization within the AMPL software. A cross-flow membrane model was used to calculate the separation. A cost model was used to express the objective function as the specific separation cost of the considered product stream. It considers capital costs of the main equipment (membranes modules, compressors, vacuum pumps, expanders and heat exchangers), and operating costs which includes operating and maintenance cost, and energy cost. The optimization of the process superstructure is performed by minimizing the separation costs expressed in EUR/Ton of CO2 or H2. Resulting process configuration is then evaluated in the Aspen Plus® software to check for overall feasibility, and to allow comparison with classical separation.

Illustration: Optimized separation architectures for CO_2 recovery from BFG under an imposed residual N_2 constraint of 0.4% and a production of 186 mol/s.



Main results

The illustration shows the resulting separation architectures for the production of a CO_2 stream with an imposed N_2 residual content of 0.4% N_2, when solutions of the optimization problem are evaluated for a maximum of two (a) and three (b) membrane stages. Separation cost for the two-stage separation was evaluated as 46 EUR/ton CO_2 while for the three-stage separation it was evaluated as 41 EUR/ton CO_2. Despite the increase in total membrane surface and the addition of an additional compressor and vacuum pumps, costs are lower, illustrating the potential of the optimization approach to develop cost-effective membrane separation processes

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2018

Membrane reactors: Methodological approach in process design

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

General context, scientific issues

Integrated processes, coupled units and intensified equipments have been largely developed in the last decades. Despite they are all used as cost minimization tools, they are not included in traditional process design approach[1].

Today, a large quantity of new process design approaches do not use the unit operation concept as a basis of the process architecture. Indeed, most of physical and chemical phenomena are treated as independent operating building blocks. The process engineer has to find the most efficient and profitable way to assemble these blocks in order to solve a reaction/separation problem and build a feasible flowsheet.

Objectives and stakes

The main objective of this project is to identify quantitative criteria and/or rules of thumb in order to choose a Membrane Reactor (MR) or a Reactor Separator with Recycle (RSR) as the best option to solve a reaction/separation problem.

A second purpose is to evaluate the global performance of every single feasible arrangement in both cases: it means to determine the recycled streams and the recycle ratios offering the highest performances.

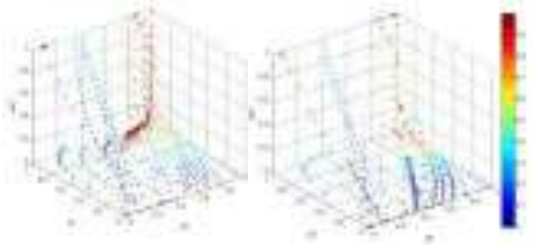
At the end, an algorithm is expected to establish in the very early step in the process design approach the relevance of an intensified operation and the arrangement needed to optimize the global efficiency.

Methodology / Experimental approach

In order to find the most interesting unit operation and the optimal recycle rates, a Matlab code has been implemented. The model includes the mathematical description of transport and reaction phenomena and the mass balances through the process superstructures. It enables the study and optimization of RM and RSR superstructures in a single step.

At first, ethane reforming was examined as a base case[2]. After model validation by comparison with the literature, input parameters were modified in order to extrapolate the results to any reaction/separation problem.

Illustration: *Optimal global efficiency for the membrane reactor (right) and the Reactor-Separator-Recycle (left).*



Main results

First, a parametrical analysis was made on the base case: it aimed to describe the sensitivity of the system when the input variables are slightly modified. By this way, the most influencing variables were identified and classified as a function of their capacity to modify the single-pass conversion, the separation efficiency and the global conversion.

Once the input variables are fixed (feed stream, reaction kinetics and membrane permeabilities), it is possible to obtain the following information from the Matlab code:

-The local performances: reactor conversion, permeate and retentate recoveries for the product and the limiting reactant.

-The global performance: defined as the total conversion through the superstructure and plotted as function of local performances (see illustration).

-The optimal recycle ratios: the superstructure can be simplified and the most interesting recycle configurations can be associated to local performances.

-Dimensionless numbers: the Damkohler and Peclet modified numbers describe the behavior of the optimal solutions in a dimensionless space[3].

Finally, the next step is the simulation of a scaled-up case in Aspen HYSYS to prove the model reliability.

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2018

Conceptual process design for the thermochemical valorization of gases from integrated steelworks

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Keywords: Steel mill off-gases, Thermochemical Valorization, Water-Gas Shift Reaction, Methane Reforming, Methanol Synthesis, Process Synthesis, Multi-Objective Optimization, Life Cycle Assessment, Green Process, Heuristic Design, Simulation, Parameter Sensitivity Analysis.

General context, scientific issues

The steel industry is the main generator of CO_2 among different industrial sectors. In this context, the VALORCO (VALOrization and Reduction of CO_2 emissions in the industry) project was launched. The VALORCO project considers different pathways of CO_2 valorization through its transformation into high added value products. This particular study focuses on the conception of a thermochemical valorization pathway of off-gases from integrated steelworks.

Objectives and stakes

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

Methodology

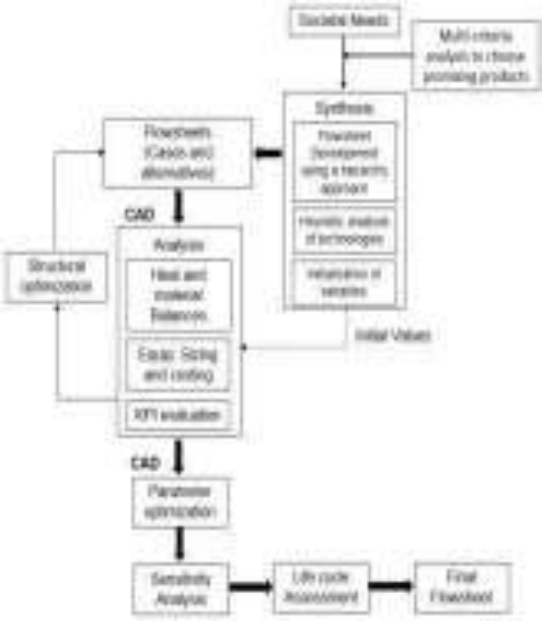
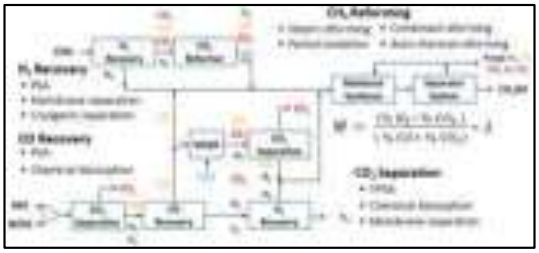


Illustration:

General structure of the valorization scenario



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

Main results

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

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

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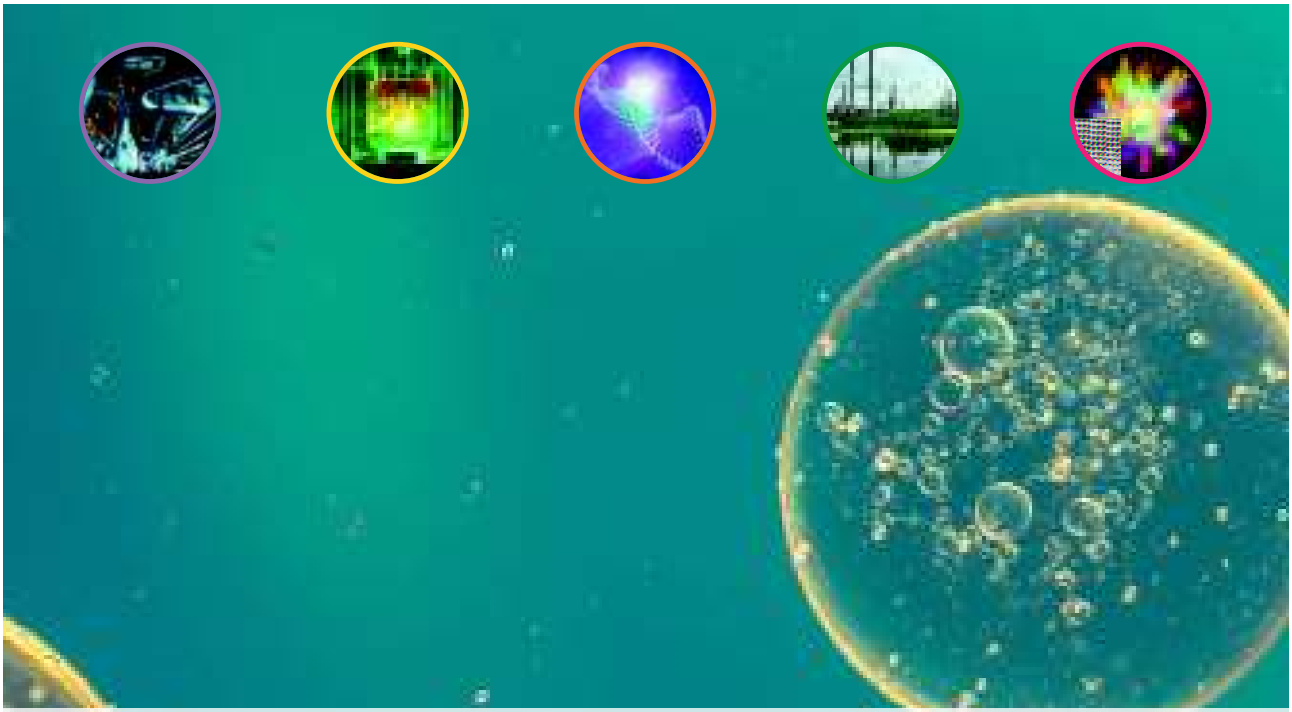
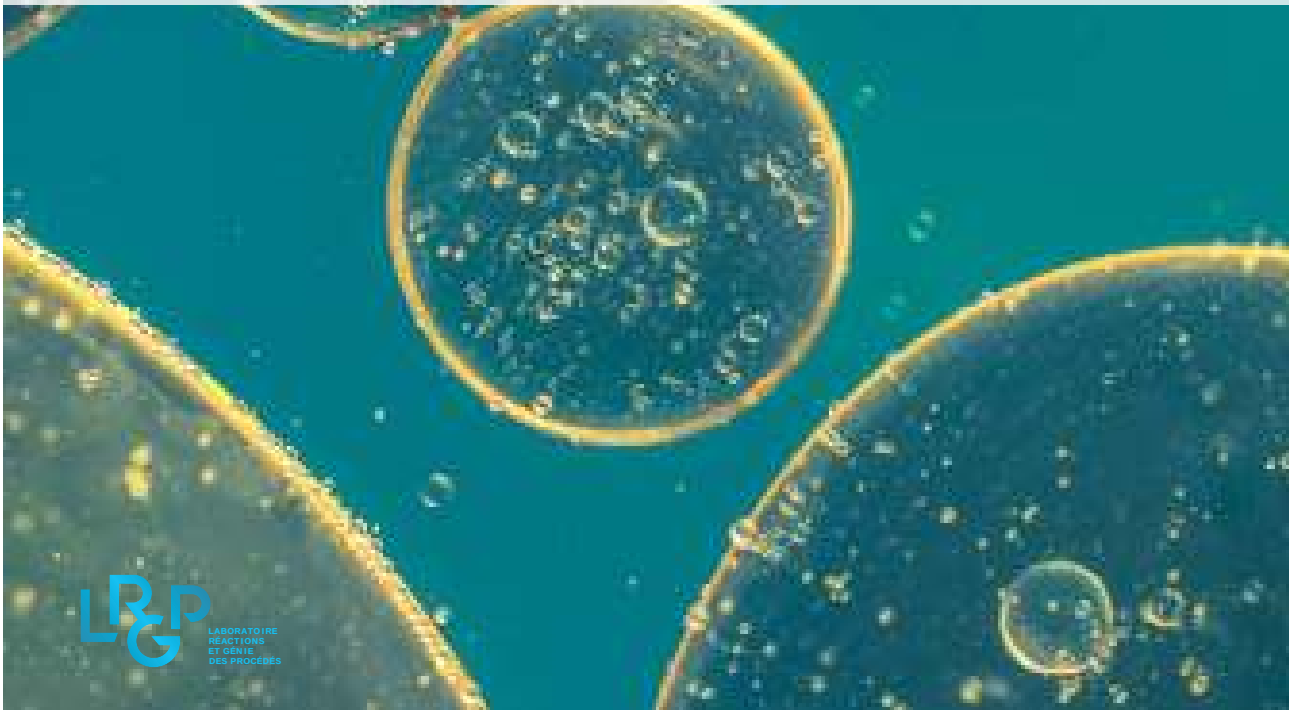


BIOPROMO

BIOPROCESS, BIOMOLECULES



2018

Development and optimization of an extrapolable process to production protein isolates from sunflower meals

Sara ALBE SLABI (3rd year)

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Axe Bioprocesses, Biomolecules | BioProMo | Avril SCA

Keywords: sunflower cake, protein, extraction, purification, ultrafiltration, size exclusion chromatography, polyphenol, quantification, modelling, optimization

General context, scientific issues

Nowadays, the world's population constantly increases. Consequently, the worldwide consumption of proteins for human nutrition is also increasing. So there is a strong need in new sources of proteins to fulfill theses needs.

Sunflower is a plant widely grown in Europe for edible oil. After extraction, a by-product (cake) rich in protein is released. At present this sunflower cake is used in animal nutrition, but the qualities of proteins might be suitable for human nutrition [1-3].

Objectives and stakes

The main drawback for the industrialization of proteins production lies on the poor extractability and the green colored of the products due to binding of phenolic compounds to proteins [1-3].

The objective of this project is to develop and optimize a process that produce colorless protein isolates with functional and nutritional properties preserved at a satisfying yield.

Methodology / Experimental approach

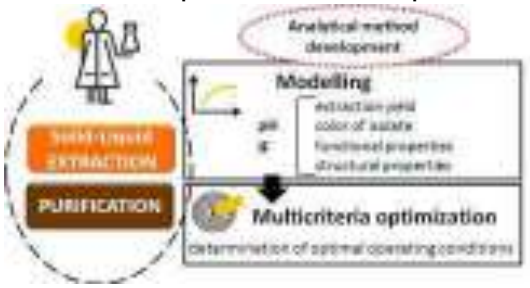
Modelling and multicriteria optimization of extraction process

The goal of this part is the identification of optimal conditions for protein extraction from sunflower cake. For this purpose, design of experiments will be achieved in order to study the impact of pH and ionic strength on extraction yield, color of powder and condition of functional and structural properties of isolate. Conditions selected by multi-criteria optimization will be retained for the next stage of project.

Modelling and multicriteria optimization of purification process

Subsequently, the study of purification process of aqueous extract using membrane ultrafiltration will be carried out. The objective is to maximize the process performance in term of purification yield, purity and color of isolate.

Strategy of modelling and multicriteria optimization of extraction and purification the sunflower proteins



Main results

For the purpose of modelling and optimization of solid/liquid extraction and purification step, a rapid and a reliable characterization of proteins and chlorogenic acid in liquid fraction was required to develop. A new method by Size Exclusion Chromatography (SEC) was validated to be specific, sensitive, precise and accurate for simultaneous quantification of proteins and chlorogenic acid in one simple run.

The first design of experiments using hexane defatted sunflower meal was also achieved. The effect of pH and ionic strength on protein extractability, solubility and phenolic contamination was investigated. However, the results clearly showed that extraction yield cannot reach the yield target value. For this reason the starting raw material was replaced by cold-pressed sunflower meal, which resulted in a significant increase of extraction yield. Furthermore, the reproduced design of experiments allowed to choose the optimal operating conditions of solid/liquid extraction.

The whole methodology is currently applied for modelling and optimization of protein purification by membrane filtration.

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2018

Improvement of rapeseed albumins digestibility and functionalities by enzymatic proteolysis

Sophie BEAUBIER (2nd year)

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Axe Bioprocesses, Biomolecules | BioProMo | Avril SCA

Keywords: Rapeseed albumins, hydrolysis, enzymes, digestibility, peptides, functionalities, modelling, chromatography

General context, scientific issues

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

Objectives and stakes

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

Methodology / Experimental approach

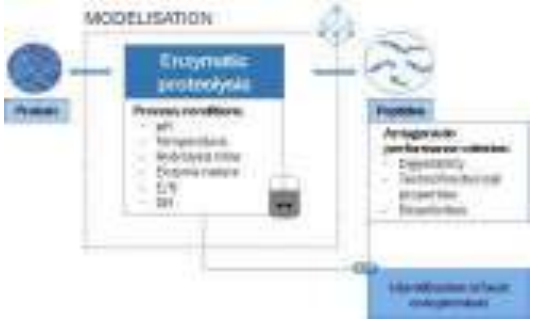
An effective monitor of the enzymatic proteolysis process requires the quantification of three parameters: the protein conversion rate, the size of peptide released and DH. An original analytical methodology to quantify simultaneously these three criteria will be developed.

A strategy of modelling the effect of the operating conditions (pH, T, E/S) on albumins proteolysis will be realized for every chosen protease. Evaluation of criterion will be done by means of the developed methodology and *in vitro* systems.

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

The process conditions of enzymatic proteolysis will be extrapolated and validation of properties with real systems will be implemented.

Illustration: Simplified scheme of general approach



Main results

An analytical methodology to quantify simultaneously the degree of hydrolysis, protein conversion rate and mean molar weight of peptides released in the course of enzymatic proteolysis has been developed. This one is based on size-exclusion high-performance liquid chromatography (SE-HPLC) analysis and on a recently published method [3]. The approach was tested on the hydrolysis of bovine serum albumin, lysozyme and rapeseed albumin with different enzymes. Results were compared to reference methods of DH quantification (TNBS and pH-stat). The proposed methodology can be efficient to study the process of enzymatic proteolysis while minimizing time and quantity of sample assay required. Moreover, this one is also used to study the *in vitro* digestibility gain after a simulated gastro-intestinal digestion.

First results of the analysis of operating conditions influence on albumins hydrolysis permit to choose 4 interest proteases. Those also allow for hydrolysis mechanism identification. pH seems to have an influence on reaction mechanism with the results to date.

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2018

Intensified & sustainable enzymatic acylation processes on innovative macroporous/mesoporous materials

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Keywords: Enzymes, acylation, supercritical CO_2, immobilized enzyme

General context, scientific issues

The N-acylation of amino acids and peptides which consists in grafting an acyl donor (fatty acid) onto the amino group of an acyl acceptor (amino acids or peptides) is currently carried out at an industrial scale via the reaction of Schotten-Baumann for the production of lipoaminoacids (LAA) largely used as biosurfactants in cosmetics and pharmaceuticals. Despite its good performance this chemical reaction unfortunately requires the use of acyl chloride, organic solvents and a high pH with salts generation that is an environmental issue. In this context, the development of soft biological processes using enzymes is considered as a potential alternative, especially since studies reported by Zaks and Klibanov demonstrating that lipases in anhydrous media can have a synthetic activity (acylation) instead of a hydrolytic activity. Since then efforts were put on the use of various non-aqueous media such as organic solvents, eutectic solvents as well as supercritical CO_2 ($scCO_2$). Some enzymes, such as aminoacylases, are also able to carry on such reactions in aqueous media.

Objectives and stakes

Because enzymatic N-acylation in non-aqueous media is quite difficult to achieve due to amino acid solubility limitations, the amino acids acylation was evaluated using aminoacylases produced at LRGP from cultures of *Streptomyces ambofaciens*,

-another goal is to evaluate the enzyme activity and stability of home-produced immobilized enzymes on macro/mesoporous siliceous supports such as SBA-15 described by Canilho and *al.* 2013 [1],

-the final objective is to generate a competitive green process for the production of LAA.

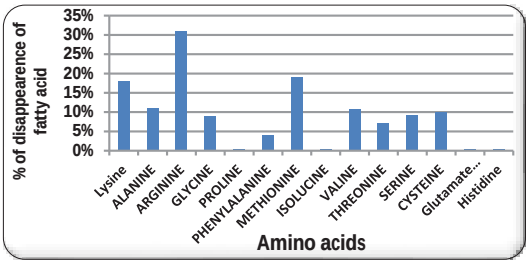
Methodology / Experimental approach

In order to evaluate the acylation of amino acids with different fatty acids, free aminoacylases were used in batch or continuous reactor using buffer as medium. These enzymes were then immobilized on mesoporous support with different APTES percentage. The activity and the stability of the immobilized enzymes were evaluated.

Illustration: Immobilization principle

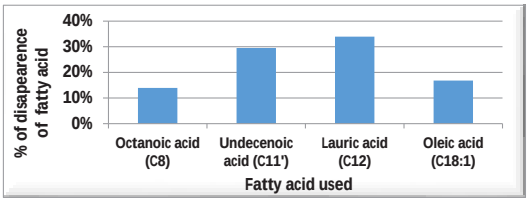
Main results

Amino acids acylation with undecenoic acid:



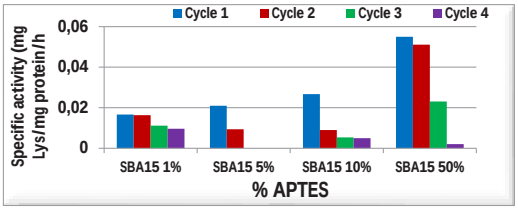
The results show that the enzyme presents a higher specificity to arginine in comparison with other amino acid substrates.

Arginine acylation with different fatty acids:



The results showed that aminoacylases are able to acylate the arginine with the four fatty acids used.

Aminoacylase activity and stability after immobilisation:



Higher is the APTES percentage better is the activity but the stability is lost after three or four runs.

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2018

Succinate production by *Corynebacterium glutamicum*: from metabolic modeling to dynamic optimization

Amani BRIKI (2nd year)

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Keywords: metabolic modelling, simulation, aero-anaerobic process, *Corynebacterium glutamicum*, succinate

General context, scientific issues

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

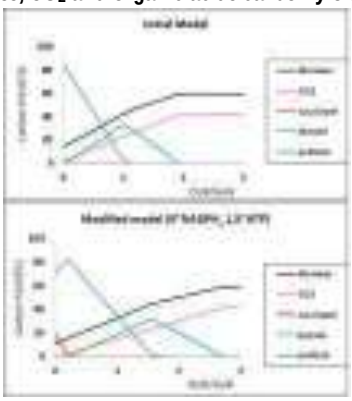
Objectives and stakes

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

Methodology / Experimental approach

Based on physiological and genetic data, a simplified model integrating central metabolism, transport and exchange reactions, and a "biomass reaction" was built. This last one is a semi-empirical reaction containing the requirement in terms of precursors and energy for the production of 1 g of biomass. Some modifications were introduced in the metabolic model (biomass reaction and some metabolic reactions) to improve the prediction of growth and organic acids production. The simulated metabolic fluxes were then compared with experimental results obtained in various conditions of oxygen (OUR) and glucose uptake rates (GUR).

Illustration: Comparison of FBA simulation with the initial and modified model: influence of OUR/GUR ratio on biomass, CO_2 and organic acids carbon yields



Main results

The influence of OUR and GUR on metabolic flux profiles was simulated using FBA. Most of the model results for the wild-type strain agreed with experimental and simulated data from the literature (1). Only the simulation of the conversion yield of glucose in succinate was not satisfactory. Based on a sensitivity study, the stoichiometric coefficients in the biomass reaction were adjusted. It was demonstrated that the production of biomass and of the succinate depend mainly on NADPH and ATP needs for the biomass synthesis. Compared with previous experimental data (2) and simulated data (1), the most convincing simulation of the metabolic fluxes was obtained by removing the use of NADPH for the biomass synthesis and by multiplying the use of ATP by 1.5. This model allowed a successful simulation of growth, consumption and production specific rates during a discontinuous process of succinate production.

References

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2018

Study of the bacterial microenvironment in a bioleaching stirred tank bioreactor: transport phenomena and kinetic modeling in three-phase flow

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Keywords: Bioleaching; Modeling; Kinetics; Stirred reactor; Simulation

General context, scientific issues

Bioleaching is an extraction method of metals contained in ores using microorganisms. Stirred tank bioreactor represents a robust method for high value-added materials and targets metals such as gold, cobalt or nickel. In order to improve the control of its parameters (physico-chemical, biological, reactor design) and thus, to increase the process productivity, it is important to develop a robust hydrokinetic model.

Objectives and stakes

The guideline of this work is to develop a hydrokinetic model of a bioleaching stirred tank bioreactor, which will be adapted as a toolbox for global simulation of the process. To this end, this work is separated into three steps:

- Kinetics modeling of a bioleaching stirred tank reactor by representing the chemical and biological kinetics as a set of differential equations and simulating them under MatLab.
- CFD (Computational Fluid Dynamics) modeling of the three-phase hydrodynamics using Fluent.
- Coupling of the above-mentioned models in a hydrokinetic simulation and degradation into a toolbox.

Methodology / Experimental approach

Kinetics modeling is focused on as the objective of the first year. Bioleaching can be represented by the kinetics of two complementary phenomena: leaching (chemical oxidation of the mineral) and biological oxidations (ferrous iron and elemental sulfur oxidations).

- Leaching is the dissolution of sulfides minerals (MS), it can be represented by a leaching rate equation [1]:

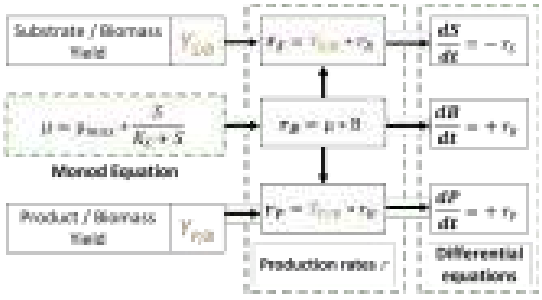
$$r_{mineral} = k(T) \cdot ([Fe^{2+}]/[Fe^{3+}])^{0.5} \cdot (1 - C)^{2/3} \quad (1)$$

- Both biological oxidations can be determined by the specific cell growth that are characterized by a Monod equation with S as substrate concentration [2]:

$$\mu = \mu_{max} \cdot [S/(K_S + S)] \quad (2)$$

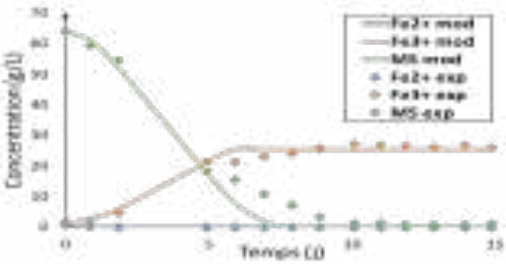
Eqs. (1) and (2) are used to describe the consumption and production rates of the components of the system. Material balance for each component is carried out to determine a system of differential equations representing the variation of the components of the system.

Illustration: Establishment of a differential equation system



Main results

The purpose of the kinetic model is to determine the system variation for a specific time step (experimentation time) and with particular conditions (initial conditions). To this end, the model was tested and fitted for BRGM experimental data, using the KCC F substrate and the KCC-E consortia:



Bioleaching kinetics are generally well represented by the model, especially for biological kinetics ($r^2 > 0.95$ for Fe^{2+} and Fe^{3+}). The difference observed in the dissolution of sulfide minerals is explained by the presence of silicate that cannot be leached and slow down the reaction. Possible spatial heterogeneities will be further simulated by CFD.

When adjusted, the kinetic model can be used for optimization purposes, to improve process efficiency.

References

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2018

Targeted PhotoDynamic Therapy

Ludovic COLOMBEAU (Researcher)

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

Objectives and stakes

- Project 1: Photosensitizers coupled to folic acid or antifolate [1].
- Project 2: Photomolecular beacon targeting LRP-1 to handle the glioblastoma by PDT [2].
- Project 3: AGuIX® theranostic nanoparticles for vascular-targeted interstitial PDT of GBM [3].
- Project 4: PDT without light via X-ray to treat deep tumor [4].

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...

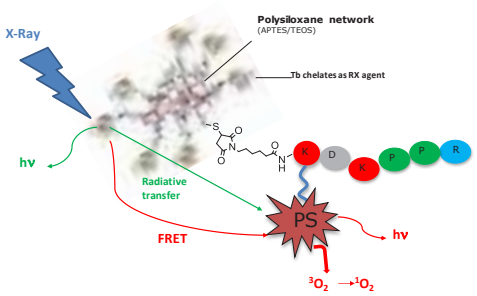
Photophysical characterization:

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

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

Uptake, dark cytotoxicity, selectivity, phototoxicity...

Illustration: Concept of the PDT without light against GBM.



Main results

- Project 1: Folic acid conjugates with 7 different photosensitizers (a pattern is accepted) and 3 antifolate conjugates with a porphyrin have been synthetized, purified, characterized and their photophysical properties studied. The evaluation of the conjugates' photostability and biological studies are under progress.
- Project 2: Peptides described in the literature targeting LRP-1 receptor and peptide-photosensitizer were synthesized and characterized. Because of the poor solubility of the compounds, news peptides and peptide-photosensitizer have been synthetized and the first biological results are performed.
- Project 3: Nanoplatforms targeting NRP-1 has been designed. Their affinity for NRP-1 have been evaluated. The *in vivo* selectivity, evaluated using a skinfold chamber in mice, confirms that the nanoparticles are localized in the tumor vessel wall.
- Project 4: The coupling of the watersoluble porphyrin to the DKPPR peptide is under progress. A photophysical study to prove the energy transfer between the nanoscintillator and the PS is under progress.

References

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2018

Development and optimization of an scalable process to produce albumin and globulin isolates from rapeseed meals

Claire DEFAIX (3rd year)

Romain KAPEL, Frantz FOURNIER
Axe Bioprocesses, Biomolecules| BioProMo | Avril SCA

Keywords: Rapeseed meal, protein extraction, purification, chromatography, ultrafiltration, multicriteria optimization, modelling

General context, scientific issues

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

Objectives and stakes

Two main challenges are to be overcome:

* The first one is to increase the protein extraction yields: so far, only 25 to 30% of the total proteins are recovered. This will be achieved by (i) applying an original strategy for optimizing the extraction step and (ii) by using innovative enzymatic treatments.

The remaining part of the extract is composed of anti-nutritional factors, such as phenolic compounds, altering the taste and colour of the final product.

* The second challenge will be to optimize a membrane based purification process in order to reach the protein isolate quality (purity over 90 %) at a minimum water cost and with the best techno-functional properties.

Methodology / Experimental approach

* Extraction

A multicriteria optimization strategy will be applied in three steps: (i) modelling the effect of the operating conditions on the process performance (protein yield, protein structure, phenolic complexation, protein functionality, powders colour) and extract composition, (ii) define Pareto zones using a diploid evolutionary algorithm [2], (iii) apply decision-making strategies to select the best trade-off operating conditions.

* Purification (Ultrafiltration)

Development of a strategy to predict the purification performances (yield, purity, productivity) according to the operating conditions and to the composition of the extracts used. This model will be based on mass balance equations [3].

Illustration: Simplified scheme of protein extraction and interest for human nutrition

Main results

* Protein extraction

Thanks to designs of experiments, optimal conditions of extraction (pH, ionic strength, temperature) were determined to obtain albumins and globulins separately: pH 4 and 0.2 M NaCl at 55 °C was shown to give the best albumin yield; pH 8.5 and no salt resulted in the highest yield in globulins.

* Development of analytical methods

An analytical method using an HPLC (High Performance Liquid Chromatography) system combined with size-exclusion stationary phase has been successfully developed in order to identify and quantify the extracted proteins. A publication is currently being written.

* Purification by ultrafiltration

The cut-off points of the membranes have been determined according to their capability to separate the proteins from the phenolic compounds. The design of experiments methodology is to be applied to determine the best operating conditions (pH, ionic strength) to purify each product, albumins and globulins, in order to reach desired performance criteria: purity (> 90 %), phytic acid content (< 3 %), lowest phenolic contamination and lowest water consumption.

References

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2018

Platforms for improving the treatment of glioblastoma by photodynamic therapy

Ludivine LARUE (1st year)

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Axe Bioprocesses, Biomolecules | BioProMo|LCPM

Keywords: photodynamic therapy, glioblastoma, peptide, alkoxyamine, Reactive Oxygen species

General context, scientific issues

Photodynamic therapy (PDT) is a simple and efficient approach to treat various malignant cancers by the use of three essential components: light, oxygen (O_2) and photosensitizers (PS). The absence of oxygen in the tissue or its deficiency due to the prior consumption by the PS presents a major drawback for PDT[1] and reduces its efficacy in killing cancer cells.

It has been proven, recently, by Audran *et al.*, that alkoxyamines R_3-ON(R_1)R_2 were useful agents for theranostic application[2]. Their ability to destroy cancer cells have been demonstrated *in vitro*[3] and *in vivo*[4]. This effect has been attributed to the production and the release of alkyl radicals.[3]

PDT also suffer of another drawback: the lack of selectivity of commercial PS. Indeed, it could happen that an illumination of a large area is necessary, for example in the case of metastases. The elaboration of new selective PS, mainly distributed in cancer cells or targeting the neovessels supplying the tumor, is essential.[5] For having an efficient PDT effect, the targeting of tumor vasculature is an attractive strategy. The receptors specifically located on the angiogenic endothelial cells, such as receptors to vascular endothelial growth factor (VEGF) or co-receptor NRP-1 can be used as molecular targets.[6] The efficient targeting of NRP-1 receptors have ever been demonstrated by our team by the use of peptides.[7]

Objectives and stakes

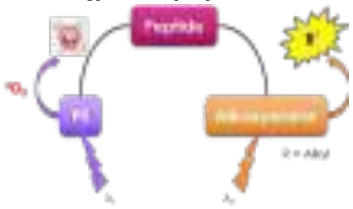
The aim of the project is the development of new innovative-targeted platforms for PDT that could work with or without oxygen. The planned strategy is the combination of three entities: a photolabile alkoxyamine (O_2-independent compound), a PS (O_2-dependent compound) and an addressing peptide. The objective is divided in three parts:

- Synthesis of the new targeted platforms,
- Investigation of photophysical properties of the PS and photolability of alkoxyamine,
- Biological investigation of platforms *in vitro* and *in vivo*.

Methodology / Experimental approach

- Organic synthesis methodology (solid phase peptide synthesis by using the Fmoc strategy) and purification by HPLC.
- Characterization of compounds by HPLC, MS, RMN ^{1}H and ^{13}C.
- Photophysical characterization: UV-visible absorption, fluorescence emission, singlet oxygen and other ROS production.
- Photolability: homolysis of the C-ON bond of alkoxyamine

Illustration: Strategy of the project



Main results

- Synthesis, purification and characterization of the first serie of compound: PS-Peptide-Alkoxyamine, PS-Peptide and Peptide-Alkoxyamine. The last two molecules were synthesized as references to compare with the first one if there is an enhancement of the PDT effect.

- Photophysical properties (quantum yields and lifetimes of fluorescence and singlet oxygen) of each compound were investigated in three solvents (water, ethanol and DMSO). A high decrease of each value was shown in water due to a lack of solubility of our compounds.

- Photolability of Alkoxyamine was observed with or without the PS and the peptide with a slightly difference of time for the complete homolysis. (Excitation wavelength = 254 et 365 nm)

- Biological properties will be further evaluated.

References

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2018

Purification and biomedical valorization of model phenolic fraction

Thi Tuong LE (1st year)

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Keywords: Phenolic, purification processes, anti-inflammatory, osteoporosis, immunity therapy, spaceflight

General context, scientific issues

This study is conducted to search the natural products such as phenolic compounds and biological evaluation coming from Oleaginous. These compounds are highly expected that they could act on osteoporosis and immune cell development during spaceflight. Nowadays, rapeseed and sunflower are the most cultivated oil containing in Europe. In fact, LRGP is currently a collaborator with AVRIL company where specially develop the industrial process for extraction/ purification of protein from rapeseed and sunflower meal. These processes leave a huge volume of permeate containing rich in phenolic compounds. Therefore, it is valuable to valorize all the components from the permeate. Indeed, several studies have showed that polyphenol have anti-inflammatory in vivo cases [1, 2]. In conclusion, this is a promising way to identify a new anti-inflammatory compounds which could induce not only the bone formation but also the immunity system.

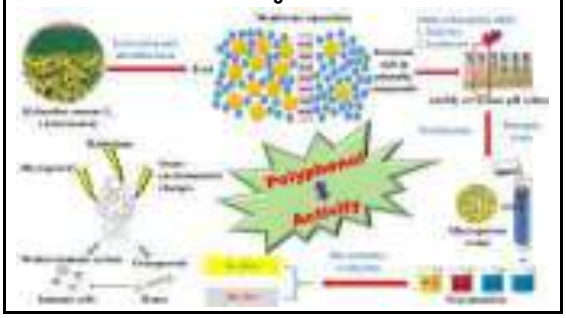
Objectives and stakes

The aim of this project is to purify and valorize polyphenols come from industrial by-products focusing on sunflower and rapeseed. To reach this goal, we are investigating in two main steps: firstly, development the extraction, purification and characterization processes. Secondly, evaluation the antioxidant, anti-inflammatory and inducing the immunity system in vitro and in vivo under spaceflight conditions as well. [3]

Methodology / Experimental approach

We divided into 2 parts to completed these goals:
1) Development of optimization and scalable process for isolating phenolic fractions. Firstly, modeling the effects of the operation conditions of separation step on the purity and yield of phenolic compounds. Secondly, we investigate the stability of polyphenol. 2) Biological activities of the phenolic fractions selected in part 1:
a) measure cell cytotoxicity and bioactivity on different cell lines; b) the phenolic fractions presenting anti-inflammatory properties and positive effects on bone formation would be administered to a murine model;
c) in vivo study: apply in the rodent model such as mice.

Illustration: General strategies



Main results

1) Screening of macroporous resins for purification of phenolic compounds

To effectively enrich the phenolic compounds, we screened the adsorption and desorption capacities of five different resins. The adsorption and desorption capacities of resins not only correlate with the physical/chemical properties but also with the pore size, specific surface area of the adsorbent. Taking adsorption/ desorption ratios and specific surface area adsorption capacity into account, we have chosen the most appropriate resin for phenolic compounds yield, purification.

2) Adsorption kinetics study

Four kinetic models pseudo-first-order, pseudo-second-order, Elovich and intra-particles diffusion were used to determine the adsorption process of polyphenol on resins. The pseudo-second-order model was the most suitable for describing the whole adsorption behavior of phenolic compounds on resins.

3) Adsorption isotherms on the resins selected

Four isotherm models Langmuir, Freundlich, Redlich-Peterson and Toth were used to describe the adsorption properties of phenolic compounds on resins. The Langmuir model was the most favorable for describing the adsorption characteristic.

References

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2018	Real-time identification and quantification of functional parameters of animal cells cultured in bioreactor by using *in-situ* spectroscopic tools **Mengyao LI (3rd year)** Annie MARC, Bruno EBEL Axe Bioprocesses, Biomolecules | BioProMo	

Keywords: Bioprocess; Mammalian cell culture; Recombinant monoclonal antibody; Glycosylation; In situ spectroscopies (Dielectric, NIR, Raman); Chemometrics; Real-time monitoring; Process control

General context, scientific issues

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

Objectives and stakes

Development of in-situ monitoring of functional parameters of producing mAbs CHO cells in bioreactor:

- **Use of spectroscopic sensors implemented in bioreactors and development of real-time prediction models for, not only, the concentration of different analytes, but also, the cell kinetic parameters, such as cell growth (μ), and the glycosylation quality of the mAb produced.**
- **Implementation of spectroscopic models to real-time control different cell culture bioprocesses (batch, fed-batch, feed-harvest), in order to reach a better understanding of the processes and a good control of the mAb quality.**

Methodology / Experimental approach

Bioreactor cell culture experiments

- In-situ experimental data acquisition by conventional (pH, temperature, dissolved O_2) and spectroscopic sensors (dielectric, Near InfraRed, Raman).

- Off-line characterization of cell populations (viable, dead, lysed), medium composition (glucose, lactate, glutamine, ammonium, LDH), and mAb (glycosylation), using HPLC, LCMS/MS, enzymatic methods...

Development / implementation of prediction models

- Model calibration by combining off-line measurements with on-line spectral data using chemometric methods.

- Model optimization by comparison and combination of different types of spectroscopic data.

- Development of real-time process control based on in-situ spectroscopies to achieve better culture performance and product quality.

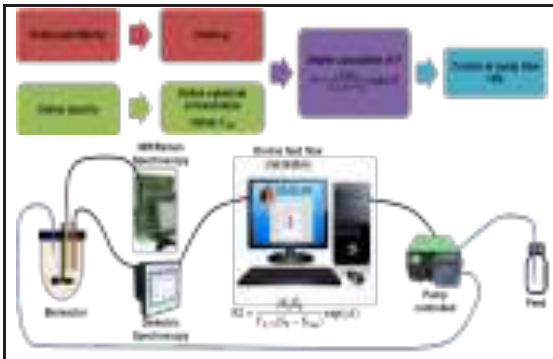

Figure 1: Online feedback control schema for feeding strategy (F) of fed-batch cultures by combining different types of spectroscopies

Main results

- **On-line prediction models were developed from in-situ NIR and Raman spectra, to monitor the concentrations of viable cells, glucose, lactate, glutamine, ammonium and mAb. Performances of both spectroscopies were evaluated in parallel with the same cultures.**
- **For the first time, one of the most important mAb quality attributes, the glycosylation (macro- and micro-heterogeneity), was successfully monitored in-situ and in real-time by Raman spectroscopy.**
- **A novel method for on-line estimation of cell specific growth rate (μ) was developed using dielectric spectroscopy. Implementation of this method in feed-harvest cultures avoided the accumulation of non-glycosylated mAb.**
- **Combining on-line models of NIR and dielectric spectroscopies allowed to successfully control in real-time the feeding flow rate of fed-batch cultures.**

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2018

Characterization and physiological impact of the hydrodynamics on expansion of human mesenchymal stem cells in bioreactors

Céline LOUBIERE (3rd year)

Eric OLMOS, Emmanuel GUEDON
Axe Bioprocesses, Biomolecules | BioProMo

Keywords: human mesenchymal stem cells, bioreactor, expansion process, hydrodynamics, microcarriers, CFD, mixing.

General context, scientific issues

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

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

Objectives and tasks

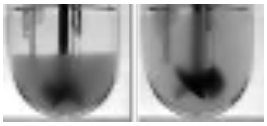
- Determination of the hydrodynamics encountered in culture bioreactors by CFD and experimental approaches (hydromechanical stress, turbulent kinetic energy dissipation, microcarrier collisions and spatial distributions).
- Impact of characterized mixing conditions on MSC expansion yield and cell quality.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

Methodology / Experimental approach

- Validation of static and dynamic expansion culture protocols of human Umbilical Cord MSC in a culture medium supplemented with human platelet lysate and investigation to identify an optimal commercial microcarrier chosen among 6.
- Development of an empirical monomial correlation based on a design of experiments with 90 $\boldsymbol{N}_{js}$ measurements varying geometric parameters (type, size and off-bottom clearance of the impeller) and the type of microcarrier (diameter and density) and dimensional analysis of the impact of these different parameters on the $\boldsymbol{N}_{js}$ value.
- Establishment of a CFD-based method to predict $\boldsymbol{N}_{js}$ and hydromechanical stress in the bioreactor (MRF Euler-Euler granular approach, k-ε turbulence model with adapted drag and turbulent dispersion force models)
- Development of a CFD-based method coupled with a multi-objective optimization and a sensitive analysis in order to predict a set of impeller designs suitable for MSC cultures with a sensitive analysis.

Illustrations

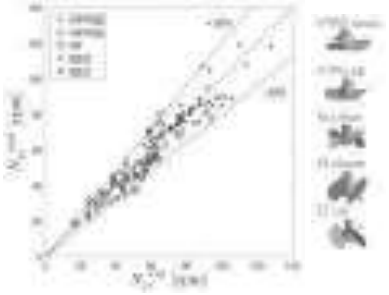
Human Umbilical Cord MSC adhered on microcarriers.



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

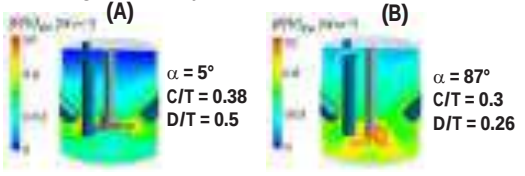
Main results

- Human Umbilical Cord MSC cultures were validated in medium supplemented with human platelet lysate, and with adapted protocols for static and dynamic conditions and revealed better yields than with Bone Marrow MSC cultures.
- An empirical monomial correlation has been established to predict $\boldsymbol{N}_{js}$ with a mean error of 8.7 %.



Comparison of experimental and modeled N_{js} according the impeller design

- Application of the CFD-based method in mini-scale bioreactors permitted to predict a set of EE down-pumping impellers designs (diameter, blade angle…) leading to lower hydromechanical stresses.



Volumetric power encountered by the microcarriers in a minibioreactor equipped with an optimal impeller (A) and a non-optimal impeller (B) at $\boldsymbol{N} = \boldsymbol{N}_{js}$.

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2018

Development of an optimized perfused-continuous process of culture of human umbilical cords mesenchymal stem cells (hMSC) grown on innovative adhesion supports

Caroline SION (1st year)

Eric OLMOS, Isabelle CHEVALOT

Axe Bioprocesses, Biomolecules | BioProMo

Keywords: human mesenchymal stem cell, bioreactor, expansion process, microcarriers

General context, scientific issues

Mesenchymal stem cells extracted from the Wharton's jelly of human umbilical cords (hWJ-MSC) show increasing interest for cell therapies due to their immunomodulatory properties, strong immaturity, high expansion capabilities, fast growth kinetics and various growth factors production capabilities.

In order to reach a high amount of cells for clinical application, it is important to develop scalable culture systems including bioprocess control and monitoring. A preliminary development of microcarrier-based cultures in Erlenmeyer's flask was realized to determine the best choices of microcarriers and culture conditions. Then, to reduce process cost and culture handlings and also to promote on-line monitoring of cell quality and cell adherence, the scale up of the process is managed in mechanically stirred tank bioreactors.

Objectives and stakes

The main objective of this work integrated into a collaborative project INTERREG project is to develop a validated innovative continuous culture process of human mesenchymal stem cells isolated from the Wharton's jelly (h-WJ-MSC). To reach this main goal, this study is divided into three steps.

* an optimization of the cell expansion in discontinuous stirred tank bioreactor by determining the most adapted set of operating conditions and surface material chemistry of microcarriers.
* a determination of experimental conditions that favour bead-to-bead transfer of hMSC in order to increase the cell expansion duration and total cell number.
* an implementation of the set of data previously optimized in a continuous-perfused mode.

As it is admitted that shear stress and physicochemical environment may affect the cell growth, stemness and functionality, it is crucial to control cell quality according to the ISCT (International Society for Cellular Therapy) criteria.

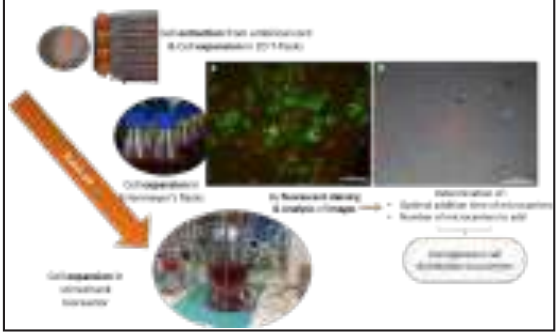
Methodology / Experimental approach

Cell extraction: Cells were isolated from umbilical cords by direct migration on surfaces avoiding the use of enzymes.

Cell culture conditions: MSC were cultivated on Cytodex-1 in HPL (human platelet lysate)-supplemented medium, in mixed Erlenmeyer's flask. After 4 days of culture, the medium was changed and each two days fresh microcarriers were added.

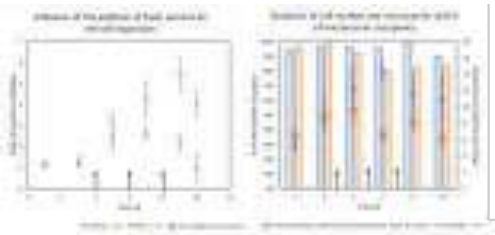
Cell counting and cell kinetics: By different fluorescent labelling and image analyses, it is possible to evaluate in situ the morphology, the viability and the colonization of the carriers. None detachment was required. Using these methods, addition of microcarrier was performed at precise moments to avoid cell aggregation. Moreover, kinetics of glucose consumption and lactate production were determined every day.

Illustration: Methodology of the process of culture of hMSC



Main results

The aim of this study is to develop an efficient process of hWJ-MSC cultures. One way concerns the control of fresh microcarriers addition by quantitative characterization of the bead-to-bead transfer.



Cell expansion appeared to be amplified by addition of fresh carriers. The procedure allowed reaching a total number of cells twice higher than without addition of carriers. Moreover, if the cell population on microcarriers is too high, cell aggregation occurred on the microcarriers, and cells began to spontaneously detach from the carriers. By analysing the number of cells per microcarrier, this number was stabilized between six and eight, whereas without addition of fresh microcarriers the number of cells per carrier increased. Based on the different pictures taken (data not shown), this addition of fresh microcarriers permitted to avoid cell aggregation and to obtain a homogeneous cell distribution on carriers.

Bead-to-bead transfer is an efficient way to improve cell adhesion and growth. A continuous-perfused mode will be developed and optimized using this bead-to-bead transfer method.

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2018

X Ray excitable multimodal nanoparticles from design to preclinical validation

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Céline FROCHOT
Axe Bioprocesses, Biomolecules | BioProMo

Keywords: nanoparticles, peptide, photosensitizer, X-ray, radiotherapy, photodynamic therapy, targeting

General context, scientific issues

Brain tumors are today one of the biggest challenges in oncology due to their very poor prognosis and the rapidly fatal outcome[1]. In the search for new diagnostic and therapeutic solutions, priority should be given to improving local control of these tumors in order to increase the rate and duration of survival of patients. In this context, the use of multimodal nanoparticles (NPs)[2] appears to be an extremely promising approach for an enhanced targeted and/or image-guided radiotherapy and photodynamic therapy (PDT)[3]. Using such NPs could allow a better targeting of receptors that are overexpressed on the surface of tumor cells or on neovessels.

Objectives and stakes

Project 1: The synthesis of peptides that target LRP-1 (Low density lipoprotein receptor-related protein) to be linked to multi-functional, X-ray excitable NPs for diagnostic and/or therapeutic purposes, for neuro-oncology applications.

Project 2: The synthesis and modification of gold (Au) NPs and nanorods (NRs) with PDT and targeting agents.

Methodology/ Experimental approach

Project 1: Functionalization for targeting LRP-1

-The synthesis of peptides for targeting LRP-1

Objective: To enhance the receptor-mediated endocytosis: All the peptides are synthesized on an automatic peptide synthesizer by fluorenylmethoxycarbonyl (Fmoc) chemistry at LCPM using coupling reagents (DCC, EDC, HATU, HBTU)

- Functionalization: Coupling of fluorescing agents to the peptide

Project 2: Gold NPs and NRs

-Synthesis and functionalization

The gold NPs and NRs are synthesized according to the literature and are coupled to photosensitizers and peptides targeting NRP-1.

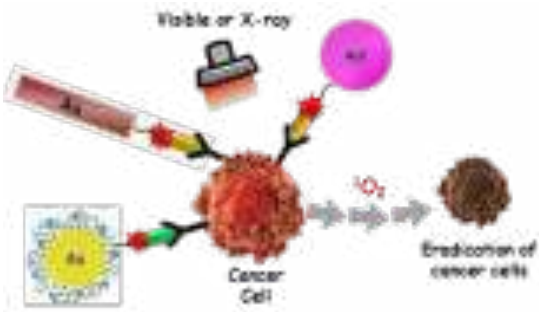
Characterizations: physicochemical and photophysical

HPLC, MS, LC-MS, zeta potential, DLS, TEM, XRD, UV-Visible absorption, fluorescence emission, singlet oxygen formation

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

Cellular Uptake, dark cytotoxicity, imaging, selectivity, phototoxicity.

Illustration:



Main results

Project 1:

Peptides for targeting LRP-1 receptor and peptide-fluorophore conjugates were synthesized. The photophysical characterizations for the elaborated molecules were performed. The primary affinity tests towards LRP-1 are under progress. The peptide-fluorophore conjugate will be then linked to the X-ray excitable NPs and finally the biological tests will be performed.

Project 2:

The AuNPs and AuNRs are synthesized and modified with polyethylene glycol (PEG) to limit their cytotoxicity[4]. The modified NPs and NRs are then covalently conjugated with a PS molecule, namely pyropheophorbide (Pyro) as a PDT agent, and with a peptide (PP) as a targeting agent. The efficient targeting of NRP-1 receptors using peptides has been thoroughly established by our team. The physicochemical and the photophysical properties of the synthesized AuNPs-PEG-PS-PP and AuNRs-PEG-PS-PP systems are studied and the obtained results reveal a prospective efficiency of those systems in PDT. The biological tests and the efficacy of the elaborated systems in PDT will be investigated in the near future.

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[4] Liu K. et al., Langmuir, 2015. 31(17): p. 4973-4980

2018

Application of *in situ* near-infrared spectroscopy (NIRS) for monitoring biopharmaceuticals production by cell cultures

Daniel ZAVALA (2nd year)

Emmanuel GUEDON, Bruno EBEL, Guadalupe AGUILAR
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Keywords: Chemometrics, mammalian cell culture, plant cell culture, recombinant monoclonal antibody (mAb), vincristine, vinblastine, Quality by Design (QbD), Process Analytical Technology (PAT).

General context, scientific issues

Since biological medicines are quite sensitive to manufacturing process, it was concluded that biopharmaceuticals process should be designed through the rules of a new quality system called Quality by Design (QbD). The main objective of QbD is to adjust the Critical Process Parameters (CPP) continuously to ensure the best Critical Quality Attributes (CQA) of the product[1]. Thus, continuous monitoring of CPP and CQA in cell culture process is required to establish advanced retro-control systems to ensure adequate control of nutrients and by-product concentrations in culture media. NIR spectroscopy (NIRS) is a promising tool in this regard since it is capable to provide multicomponent information directly without sample treatments. Nevertheless, NIR spectra is complex and multivariate calibration methods are required to properly extract and relate the observed spectra[2], in a predictive manner, to a desire variable property, such as nutrients and by-product concentrations or CQA of biological medicines.

Objectives and stakes

Under the QbD approach, the main objective is to provide and evaluate multivariate platforms to properly analyse some CPP and CQA of biopharmaceutical producing cell cultures (CHO cells and *C. roseus* cells) using *in situ* NIR probes.

Methodology

Cell cultures experiments:

- Generation of *C. roseus* plant cell lines: Characterization and establishment of culture conditions to produce anticancer molecules (vincristine-VC, vinblastine-VB).
- Bioreactor cultures: Experimental data acquisition by on-line techniques (*in situ* NIR probes) and off-line analysis.

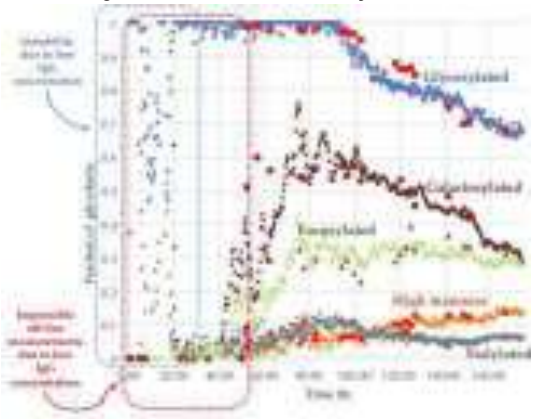
Development of calibration models:

- Use of multivariate platforms (PLSR, PCR, LWR, ANN and SVR) to generate calibration models of critical compounds.
- Enhancement of models by proper tuning.
- Evaluation of models using internal validation approaches.

Evaluation of enhanced models:

- Assessment of robustness by modification of physical and chemical conditions, using external validation approaches.
- Discussion on the nature of the cell lines for the validation of models.

Illustration: Monitoring of mAb micro-heterogeneity during CHO cells batch culture by *in situ* NIRS



Main results

Cell cultures experiments:

- Five plant cell lines have been developed and characterised
-Production of VC and VB is confirmed in *C. roseus* suspension cultures.
- Some bioreactor cultures of CHO and *C. roseus* cells have been performed.

Development of calibration models:

- Calibration models for viable cells, glucose, lactate, ammonium, glutamine and IgG concentrations have been developed and enhanced using different multivariate platforms (PLSR, PCR, LWR, ANN and SVR)
-The presence of non-linear surfaces during cell cultures has been proven, especially to monitor IgG quality and viable cells.
- Monitoring of IgG quality in terms of macro-heterogeneity and micro-heterogeneity by *in situ* NIRS calibration models has been proven feasible using non-linear regression approaches.

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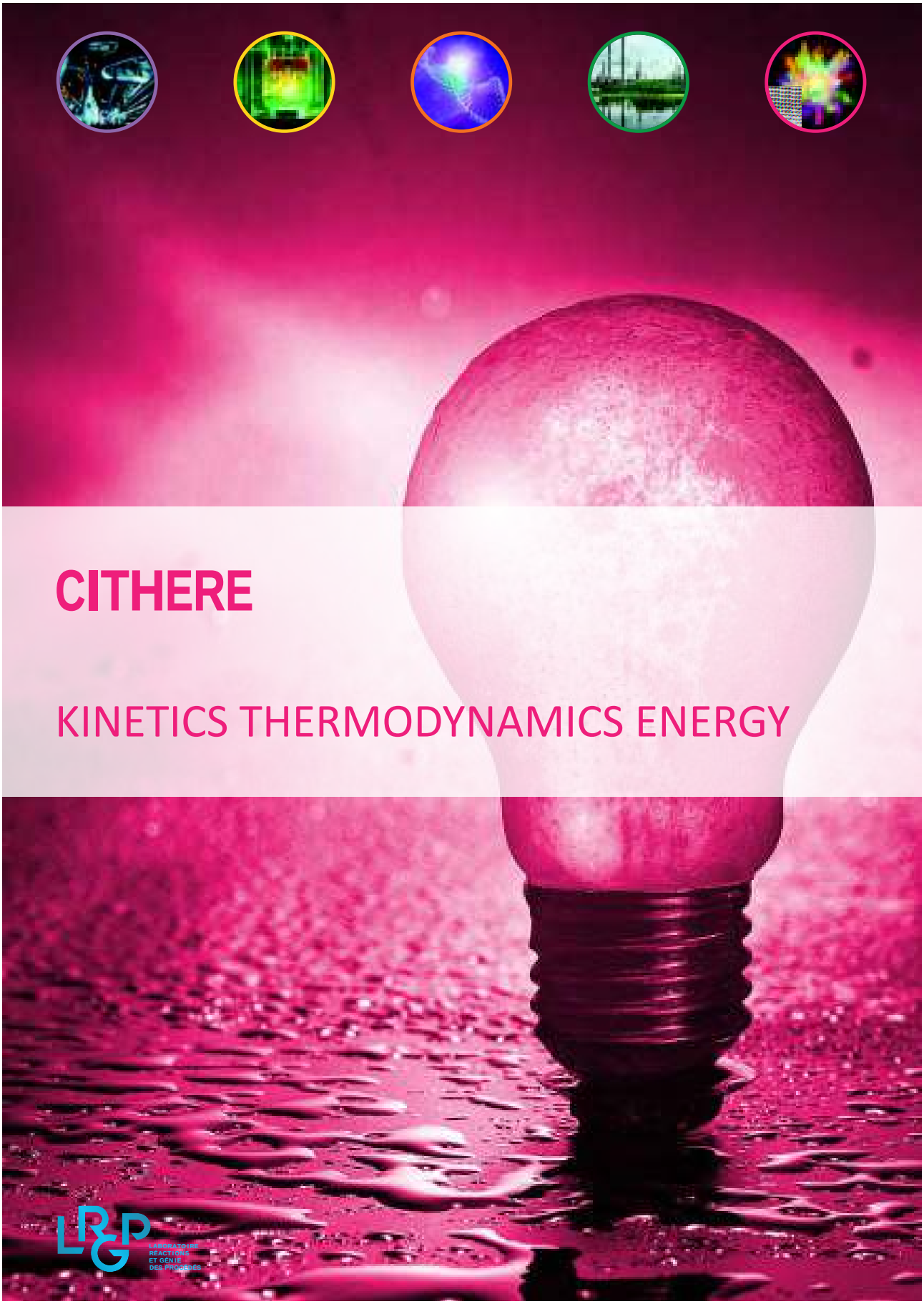

CITHERE

KINETICS THERMODYNAMICS ENERGY

LRGP
LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

2018

Biorefinery: lignin liquefaction to produce green aromatic chemicals

Erika BARTOLOMEI (1st year)

Anthony DUFOUR, Yann LE BRECH
Axe CiTherE | GREENER

Keywords:

Bioengineering, biorefinery, catalysis, lignin, biomass

General context, scientific issues

Biomass is the main sustainable source of renewable carbon. Its valorization in biorefineries leads to climate change mitigation and to the production of biofuels and green chemicals with a lower environmental impact than crude oil.

Biomass is mainly composed of lignin and carbohydrates. Lignin is the most abundant renewable resource of aromatic compounds on earth. Therefore, its valorisation is one of the most promising ways for the substitution of fossil resources to produce "green" aromatic compounds. Indeed, they can be important building blocks for producing various chemicals and materials.

Objectives and stakes

The goal of this Ph-D is to optimize lignin conversion into aromatics. It's part of an important national project gathering partners from pulp and papers industry, biorefinery, catalysis, chemical engineering and polymer science.

This project is innovative and ambitious according to different aspects:

- process engineering: the proposed process concept is new for lignin and could also be adapted to other;
- catalysis: we propose the development of green catalysts, low toxicity and inexpensive;
- for chain evaluation: it would be the first to evaluate from an environmental/techno-economic point of view the potential of the "wood-phenol" sectors in France on actual cases (functioning pulp mills).

Methodology / Experimental approach

The first study is a complete analysis of the most important industrial lignins: elementary analysis, chromatography, NMR, ATG, DSC...

Then catalytic liquid conversions will be performed in a high pressure reactor.

The products will then be analyzed to determine the efficiency and selectivity for different reactive system (solvent, catalyst, temperature, atmosphere)

Main results

Being a new project, just started, only the elementary analyzes were done on the different kinds of lignins that will be used in the process.

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Illustration :

2018

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

Felipe BUENDIA (Design engineer)

Emmanuel GUEDON(1), Anthony DUFOUR(2)
Axe CiTherE | GREENER (2) | BioProMo(1)

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 CO_2 releases into the atmosphere. A replacement source is now required. Lignocellulosic biomass presents an interesting alternative, as renewable carbon based energy sources, which respects to the environment. This project seeks the valorization of cellulose and derivatives through an efficient coupling of cellulose thermochemical conversion and fermentation processes.

Objectives and stakes

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

Methodology/ Experimental approach

This work has two stages:

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

Thermochemical conversion

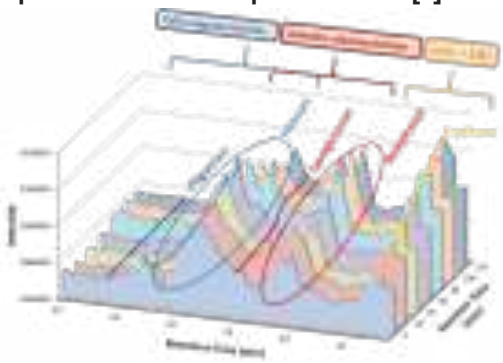
- Pyrolysis
- Liquefaction
- Analysis: HPAEC-PAD

Batch Fermentation

- Growth kinetics
- Metabolite analysis: HPLC-UV-RID

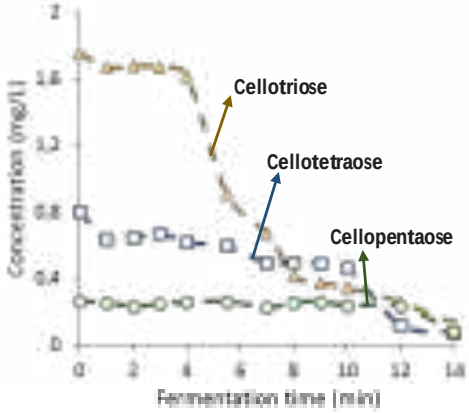
Main Results

Different products identified after cellulose liquefaction in hot-compressed water:[1]



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

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



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

References

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2018

Projet SEPIA (Solvant Eutectique Profond Innovant pour l'Absorption) Application of deep eutectic solvents as absorbent in working fluid for absorption chiller.

Laëtitia CESARI (ATER)

Fabrice MUTELET
Axe CiTherE | ThermE

Keywords: Absorption heat pump, chiller, deep eutectic solvent, CO_2, energy valorization.

General context, scientific issues

Absorption heat pumps are devices that can be used as chiller. The classical working mixtures used in such apparatus are {H_2O + LiBr} and {H_2O + NH_3}. Yet, the possible crystallization of LiBr limits the operating conditions and the {H_2O + NH_3} mixture requires to work at high pressure. Moreover, this system is toxic and not environmental friendly. [1]

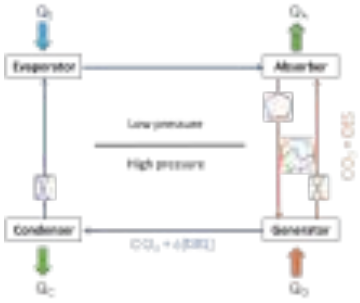
Objectives and stakes

The goal of this project is to investigate new working fluids composed of Deep Eutectic Solvent (absorbent) and CO_2 (refrigerant). Deep eutectic solvents (DESs) are noted to be green ionic liquid analogues, and their many favorable properties made them interesting for the scientific community. [2] This class of solvents is also easier to prepare, cheaper and less toxic than ionic liquids. [3] Unfortunately, there is a lack of knowledge on the behavior of deep eutectic solvents with gases. So the purposes of the project is two-fold: measurement of the thermodynamic properties of the systems {Deep Eutectic Solvent + CO_2} and the evaluation of their performances as working fluids in an absorption chiller.

Methodology / Experimental approach

The project is divided into three steps:
- Measurement of thermodynamic properties of the pure compounds and the mixtures (vapor – liquid equilibria, heat capacity and density).
- Adjustment of Peng-Robinson thermodynamic parameters on the experimental data.
- Evaluation of the performances of the working fluid in an absorption chiller: study of the influence of the heating sources and wells on the cycle 's coefficient of performance.

Illustration: Schema of an absorption chiller cycle [4]



Main results

If the performances of this system are equals or higher than the usual working fluids, the mixture {Deep Eutectic Solvent + CO_2} could constitute a very interesting alternative. The study of other deep eutectic solvents mixed with CO_2 or other refrigerant could also spread the operating range of temperature and eventually improve the cycle's performances. Moreover, this study leads to new trails of innovative working mixtures for absorption heat pump and chiller.

References

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2018

Modelling the two-phase flow for the storage of Liquefied Natural Gaz (LNG)

Aghilas DEHLOUZ (1st year)

Jean-Noël JAUBERT, Romain PRIVAT, Yongfeng QU

Axe CiTherE | ThermE | Funding by GTT (Gaztransport & Technigaz)

Keywords: Fluid mechanics, Heat transfers, Thermodynamics, Phase change, OpenFOAM, Thermo-physical properties and composition.

General context, scientific issues

The complexity of the physical phenomena observed in LNG containment systems designed by GTT requires a detailed modelling of LNG behavior taking into account the dynamic, multiphasic, multi-spices and multi-scale aspects in the establishment of physical law and models.

Objectives and stakes

For a better prediction of the LNG behavior, a new methodology has to be developed coupling thermodynamic models and three-dimensional computational fluids mechanics simulations (3D CFD).

The objective of this study is to improve current models in order to minimize their weaknesses by combining movement equations and equations of state which the aim of accurately predicting the evaporation rate, the evolution of composition and many other aspects.

Methodology / Experimental approach

This thesis can be divided in five principal steps:

i)- Post processing of the experimental data

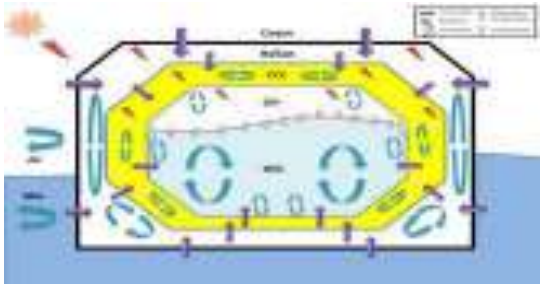
ii)- Setup an appropriate standard CFD model in OpenFOAM

iii)- Establish a complete thermodynamic model and validate its accuracy for the different properties of LNG

iv)- Implement the thermodynamic model in the CFD solver in such a way to reach a good accuracy without a consequent increase of calculation time

v)- Simulate the different experimental cases (reduced scale and real scale tanks) with the new solver and compare results to experimental data.

Illustration: Global Phenomena in an LNG tank



Main results

Generally, due to high calculation coast of 3D CFD studies and the complexity of coupling both concepts, modelling the physical properties is somehow neglected or simplified despite of the primordial role of this aspect in fluids behavior.

Indeed, in the common available studies, several phenomena have never been taken into account. Among them we have the movements generated by the sea or the aging of the LNG and the variation of its composition which has a considerable impact on the evaporation rates. Combining equations of state and conservation equations (mass, momentum and energy) should allow a good follow-up of these phenomena.

Perspectives:

--Development of a new accurate solver in OpenFOAM adapted for GTT studies

--3D simulations for different conditions and geometries

--Correlate transfer phenomena (mass, energy) in order to develop more simplified models

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2018

Hydrogen Production from Biomass and Waste Gasification, Techno-Economic Assessment of Innovative Solutions

Rémi DEMOL (Research Engineer)

Guillain MAUVIEL, Yann ROGAUME
Axe CiTherE | GREENER | LERMAB

Keywords: gasification ; biomass ; Refused Derived Fuel ; techno-economic assessment ; process simulation.

General context, scientific issues

In the context of global warming and development of renewable energies, important issues have to be answered to make these sustainable energies more affordable compared to fossil energies. Biomass and Refused Derived Fuel (RDF) gasification is identified by the French agency ADEME as an important supplier of renewable gas for the next decades [1]. Gasification consists in a partial oxidation of feedstock to produce syngas (and char). Syngas is mainly made of hydrogen, carbon monoxide, methane and carbon dioxide. Yet, a lot of undesired species are also produced during this thermal process which penalize economical viability for the subsequent steps and for regulations [2].

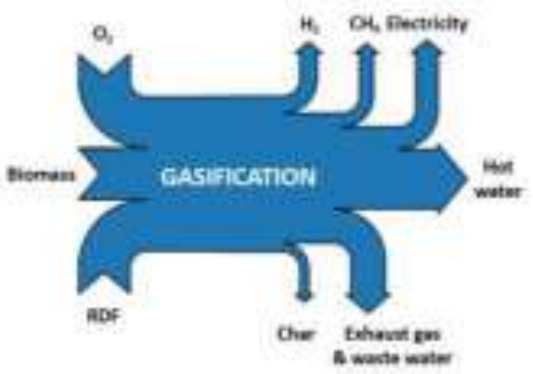
Objectives and stakes

This project will provide guidelines to determine the most economical processes to upgrade the syngas produced, from which hydrogen could be extracted along with other valuable products.

Methodology / Experimental approach

In order to get detailed data to build this techno-economic assessment, process simulation software, as Aspen Plus, are powerful tools to combine several unit operations along a process. In-house codes can also be included. Gasifier have been studied in several publications [3,4]. Nonetheless, downstream gas cleaning process is not as well established. These simulations should provide cost estimation of CAPEX and OPEX (including utilities and feedstock). This project focus on small unit of 10 MW of biomass. These kind of unit seems more appropriate for their modularity, the smaller area of supply required and also for social acceptability purpose. This project will try to maximize the efficiency by upgrading every product: heat and syngas to produce electricity and pure hydrogen, so as to overcome the small size of the unit compare to bigger plant. The impact of feedstock will be considered: biomass and RDF will be investigated. Several gas cleaning paradigms have been proposed so far: (i) cold gas cleanup, (ii) hot gas cleanup, (ii) warm gas cleanup [2].

Illustration:



Main results

This project should:

- evaluate the potential of small gasification units following an objective criterion when several products are involved: Net Present Value,
- identify upgrading ways for secondary products following circular economy principles,
- develop cleanup process to manage all potential pollutants, especially coming from RDF gasification so as to respect regulations.

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2018

Detailed chemical modeling of biomass combustion in domestic heating appliances in order to reduce their polluting emissions

Amal DHAHAK (3rd year)
LRGP: Frédérique BATTIN-LECLERC, Roda BOUNACEUR and Olivier HERBINET,
CSTB: Céline LE DREFF, ADEME: Florence PROHARAM
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Keywords: Biomass, Combustion, Pyrolysis, Kinetics, heat transfer, Modelling, Emissions

General context, scientific issues

Dwindling fossil fuel reserves and global climate change drive researchers to discover and develop strategies to derive energy from renewable sources like biomass. Wood energy is a carbon-neutral renewable energy, provided that the forests from which the wood is grown are managed in a sustainable manner. However, the combustion of wood is not free of defects. Poorly controlled, wood burning can be a source of atmospheric pollution.

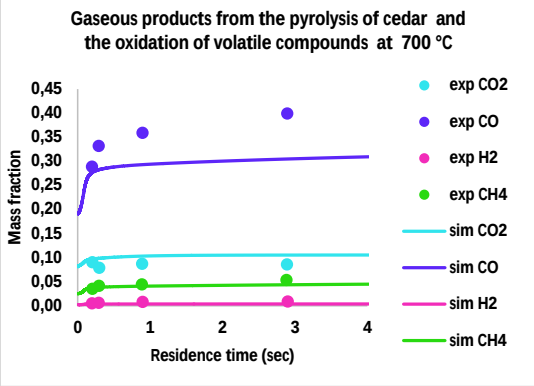
Objectives and stakes

This thesis aims to understand and model the chemical mechanisms of biomass combustion in domestic heating appliances in order to reduce polluting emissions. The main purpose of this work is to develop a model that will couple a physical approach describing thermal transfer with a detailed chemical model to reproduce the formation of pollutants in the gaseous phase. This chemical model will be based both on globalized reactions to simply represent the devolatilization of biomass and on detailed kinetic models to describe the evolution of species in the gaseous phase.

Methodology

The biomass is characterized as a mixture of three so-called reference constituents: cellulose, hemicellulose and lignin. The decomposition of biomass is therefore the combination of the pyrolysis of these three compounds. Each biomass compound is represented by a reference species. Cellulose (CELL) is represented by the monomer ($C_6H_{10}O_5$). Xylan ($C_5H_8O_4$) is the monomer chosen for hemicellulose (HCELL). Lignin, having a complex structure, is represented by three reference compounds LIGC, LIGH, and LIGO (richer in C, H and O, respectively). The decomposition of wood is therefore the superposition of degradation of its compounds. It gives a large number of liquid, gas and solid species. These compounds will undergo secondary reactions to give rise to other species.

Illustration: Simulation performed during this study [1]



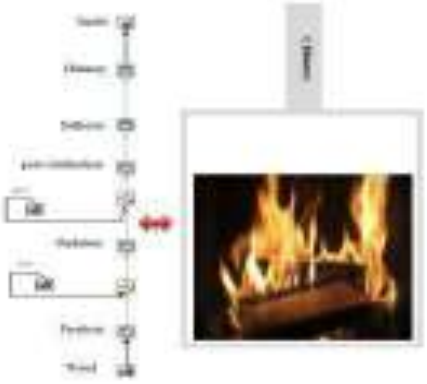
Main results

kinetic mechanism development: *LRGP BioPOx

We constructed a global model of primary pyrolysis and secondary pyrolysis and / or combustion with a special focus on some key compounds that play an important role during wood degradation. The ***LRGP BioPOx*** mechanism has been tested on several experimental points to validate it.

*** Model of thermal transfer in a wood log**

We developed a model of heat transfer and we coupled it with ***LRGP BioPOx*** to describe the wood combustion in a stove represented by a chemical reactor network.



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2018

Pyrolysis of polyethylene terephthalate: experimental study and kinetic modelling

Asma DHAHAK (2nd year)

Valérie BURKLE-VITZTHUM, Guillain MAUVIEL

Axe CiTherE | GCR/GREENER

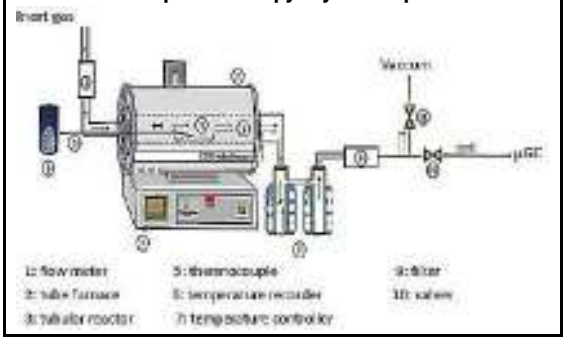
Keywords: pyrolysis, kinetic modelling, PET, thermal process, polymer materials, experimentation

General context, scientific issues

Pyrolysis is an interesting upgrading way to convert solid waste into useful gaseous, liquid and solid products (fig. 1). The solid chosen in this study is the polyethylene terephthalate (PET). Its chemical structure is in fig. 1. This polymer is widely used to make synthetic polyester fibers, packaging materials, films, electronic equipment, automotive products...(1).

Fig. 1: The structure of PET.

Illustration : Experimental pyrolysis setup



Objectives and stakes

The long-term goal of this research is to develop a detailed kinetic model of PET decomposition. However, the objective of the current study is to provide a temporal evolution of the heavy species obtained during PET pyrolysis. Particularly, the study has the following sub-objectives:

1. Identifying the pyrolysis products and analyzing the complex gas mixtures evolving from the thermal decomposition;
2. Determining the temperature pyrolysis range and studying its influence on decomposition products;
3. Better understanding the polymer behavior under high temperature.

Methodology / Experimental approach

The polymer degradation was studied in a horizontal tubular reactor that allows recovering the different pyrolysis products. In this reactor, the samples were heated up to various temperatures: 683 K, 703 K, 723 K and 753 K and hold on for 120, 90, 60, 60 min respectively. The heating rate was set at 5 K/min and the inert gas flow rate was 600 NmL/min. The sample temperature was measured during the heating period and the isothermal stage.

Three types of products were obtained: a solid residue that remains in the sample holder, a waxy product which is condensed and volatile species. These volatile species were quantified on-line by micro-Gaseous Chromatography (GC) coupled with a Thermal Conductivity Detector (TCD).

Main results

In order to more accurately understand the sample behavior throughout the pyrolysis, the sample temperature was measured and the temporal evolution of the temperature derivative was calculated. As results, the melting point is around 513 K. The maximum pyrolysis is clearly observable for 723 K and 753 K. It is around 700 K.

The waxy product was in a powder form and the solid remaining in the quartz boat was a dark residue.

The effect of final temperature on product yields was discussed. The solid residue yields exhibited no remarkable difference when the final temperature increases. It means that there are no secondary reactions that affect the loss of solid residue.

In addition, there is only a slight difference between the total gas yields. This might be explained by the fact that the gas residence time inside the reactor is only 0.78 s. This short time led to minimize the secondary reactions in gas phase.

On the other hand, the temporal evolution of major volatile species was determined. The final temperature accelerates the gas release when it goes from 683 to 703 K, but for higher temperatures, there is no major change.

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2018

Kinetic study of ester biofuels in flames

Artem DMITRIEV (2nd year)

Pierre-Alexander GLAUDE, Denis KNYAZKOV
Axe CiTherE | GCR

Keywords:

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

General context, scientific issues

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

Objectives and stakes

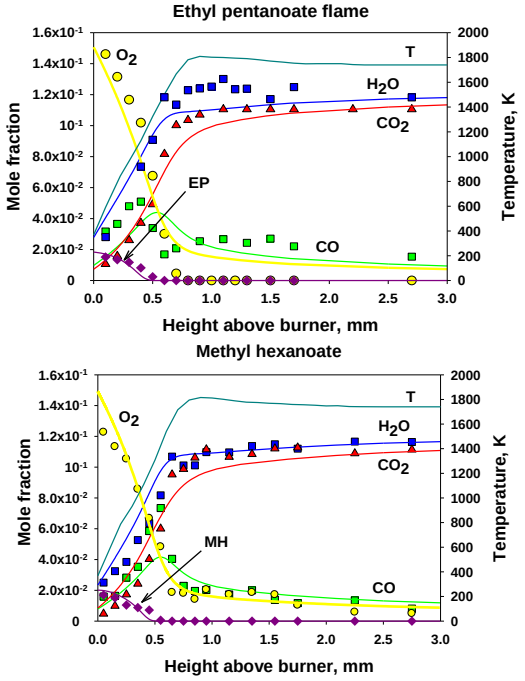
Premixed stoichiometric and fuel-rich flames (fuel/O_2/Ar) stabilized on flat burners at low (50 Torr) and atmospheric pressure fueled with the following compounds are scheduled to be studied:

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

Methodology / Experimental approach

- Gas chromatography (GC) at low-pressure conditions (LRGP, Nancy) [1]; this technique permits a quantification of the stable products and an easy separation of the isomers. A thin probe, which induces less thermal and flow perturbation in the flame, will be used.
- Molecular-beam mass-spectrometry (MBMS) with soft ionization by electron impact at atmospheric pressure (ICKC, Novosibirsk) [2]; this technique permits to measure mole fraction profiles of unstable products due to a sonic probe.

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



Main results

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

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

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2018	Valorization of biomass and wastes by gasification: optimization of the process efficiency, characterization of the various products and development of gas cleaning processes. Maxime HERVY (Research engineer) Guillain MAUVIEL, Anthony DUFOUR Axe CiTherE	GREENER	

Keywords: Biomass and waste valorization; Refuse Derived Fuel; Pyrolysis; Gasification; Tar cracking; Catalytic and thermal cracking; Fly ash valorization; Hot filtration; Characterization of char, gas, tar and soot.

General context, scientific issues

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

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

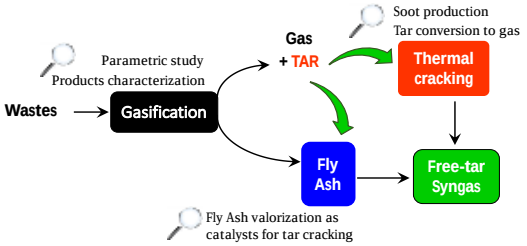
Objectives and stakes

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

Methodology / Experimental approach

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

Illustration: Scheme of the waste gasification and tar removal processes (thermal cracking, and catalytic cracking over fly ash).



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

(3) Nitrogen compounds are a significant issue for the syngas valorization processes. Fate and behavior of nitrogen compounds during the gasification of N-polluted wood wastes (glulam, board) will be studied in the ADELITHER project. This project involves two industrial partners: Leroux & Lotz Technologies, and RAGT Energie.

(4) During waste gasification in fluidized bed, the main part of the inorganic species are recovered at the gasification reactor outlet and are named fly ash. As waste can be composed of 30-50 wt.% ashes, a significant amount of fly ash can be generated during gasification. To avoid the costs associated with the fly ash landfilling, new valorization routes must be identified. This project aims to reuse fly ash as catalysts for tar cracking reactions in order to increase the syngas quality.

2018

Accurate and reliable calculation of thermodynamic properties of air-components mixtures, CCS fluids, hydrogen and innovative working fluids for closed power cycles

Silvia LASALA (Researcher)

Jean-Noël JAUBERT, Romain PRIVAT
Axe CiTherE | ThermE | Air Liquide

Keywords:
Thermodynamic models, ortho-hydrogen and para-hydrogen, air-component mixtures, CO_2 Capture and Storage (CCS) fluids, closed power cycles working fluids, working fluid design

General context

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

- cryogenic/refrigerated phase-separation processes for the purification of either air mixtures or fluids treated by CO_2-capture technologies;
- catalytic processes for hydrogen liquefaction **(ortho- and para-hydrogen);**
- closed power cycles **(inert and reactive working fluids).**

These three main areas of research are developed in the context of the activities of the team ThermE of LRGP and they are described herein.

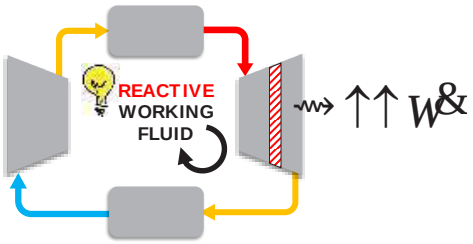
Targets, methodology and results

The activity "thermodynamics of fluids treated by cryogenic/refrigerated phase-separation processes" has already brought the following results.

- The first part of my post-doctoral studies, funded by Air Liquide, has led to: (1) attest the superiority of GERG-2008 EoS in the calculation of air-component mixtures; (2) the development of a computational Fortran code based on GERG-2008 EoS, with a complete set of robust flash algorithms (PT, PH, PS, Pz, Tz, TH, TS, UV, SV, PV) and its coupling with Simulis Thermodynamics;
- Researches over the study of thermodynamic properties of fluids treated by CO_2-capture technologies have led to the definition, optimization and application of an advanced and accurate equation of state for fluids treated by CO_2-capture processes, in particular composed of CO_2, N_2, Ar, O_2, CO, CH_4, H_2O, H_2S, H_2.

The activity "catalytic processes for hydrogen liquefaction" originates from topical industrial need of storing liquid hydrogen. In particular, the research has been devoted to the study of the thermodynamics of the reaction ortho-hydrogen ⇄ para-hydrogen and to the characterisation of the catalytic activity of ferric-oxide catalysts, in accelerating the rate of reaction of the ortho-hydrogen ⇄ para-hydrogen conversion.

Further researches



The possibility of adapting the working fluid to each application represents one of the greatest degree of flexibility to reduce the irreversibilities of closed power cycles and, thus, to maximise their efficiency and optimize their design. Despite the pivotal role represented by the optimal selection of the working fluid, the scientific knowledge level on physicochemical thermodynamic and transport properties, thermal stability and environmental characteristics of fluids does merely allow the reliable utilisation of pure-component fluids.

The activity focused on the "design of working fluids for closed power cycles" aims, firstly, to address the main scientific gaps which currently limit the assessment of the energy potential of closed cycles operating with inert and reactive mixtures as working fluids and, secondly, to evaluate such a potentiality.

The project aims at developing both a theoretical methodology and an experimental set-up to enable the optimal design of mixtures by means of, respectively, reliable thermodynamic property calculations and thermal stability measurements of inert and reactive working fluids for closed thermodynamic cycles.

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2018

Study of the influence of the additives chemical structure on the control of high and low temperature reactivity by multi-scale modeling approach

LE Minh Duy (1st year)

Pierre-Alexandre GLAUDE

Axe CiTherE | GCR | IFP Energies nouvelles

Keywords: Fuel additives, kinetic modeling, auto-ignition delay time, shock tube, rapid compression machine, autoclave

General context, scientific issues

Novel combustion systems imply new physical constraints for better performances. This encourages the use of additives to adjust fuels properties. Until today, the effect of additives has not been fully understood. It depends not only on additives (for example: chemical structure, doping level) but also on the chemical composition of fuel[1]. Moreover, multiplying fuel additives may be problematic for logistics and may generate adverse effects or uncontrolled responses in both the gas and the liquid phases under alternative engine operating conditions.

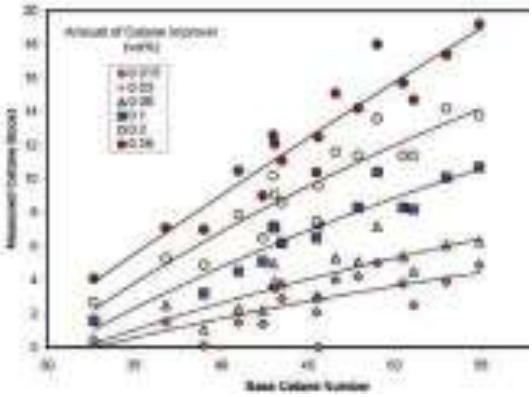
Objectives and stakes

This study aims to better understand the influence of the chemical structure of additives on the control of reactivity for a wide range of temperature

Methodology / Experimental approach

A multi-scale modeling approach including literature data assembly, automatic mechanism generator and quantum chemistry calculations is considered in order to evaluate the kinetic of additives decomposition and interactions with various fuel surrogates. Based on these results, detailed kinetic mechanisms will be developed and validated with experimental data dedicated to the characterization of the chemical effect of additives. Three experimental setups are targeted: (1) a shock tube for the high temperature reactivity; (2) a rapid compression machine for the intermediate temperature and finally (3) an autoclave designed for liquid phase studies.

Illustration: Cetane boost as a function of the cetane number of the base fuel [1]



Main results

Both the experimental investigation at high temperature and the modeling work were performed. The developed detailed chemical kinetic mechanism describes the interactions of a surrogate fuel including toluene and n-heptane with a gas phase reactivity enhancer additive (2-ethylhexylnitrate). Mechanism performances are compared with recently published mechanisms which are capable of simulating complex interactions including heavy hydrocarbons (C_7) and nitrogen containing species. Ignition delay times measurements were simultaneously performed in a shock tube (10 atm, 1350 – 1600 K) for a doping level of 100 ppm. The future work will be dedicated to the validation of the mechanism in order to discuss the additive chemical effect.

References

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2018

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

Yohann LE GUENNEC (4th year)

Jean-Noël JAUBERT, Romain PRIVAT

Axe CiTherE | ThermE | Funding by TOTAL

Keywords: Phase equilibrium, cubic equations of state, pure compounds, mixing rules

General context, scientific issues

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

Objectives and stakes

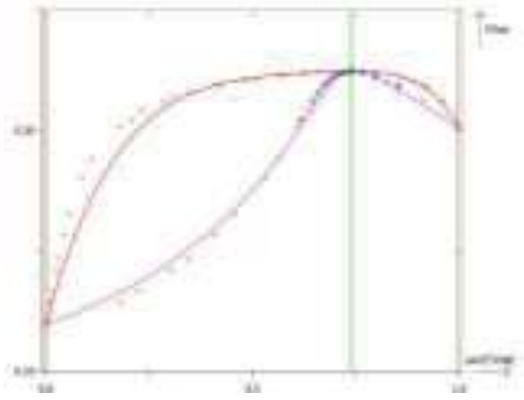
The new cubic equation of state to be proposed should be able to represent pure compounds but also mixtures of variable complexity, including ideal and non-ideal systems and non-associated and associated systems. The selection of the optimal mixing rule for the thermodynamic model will be analyzed in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

Methodology / Experimental approach

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

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

Illustration: *representation of the binary system acetone / cyclohexane at 298.15 K by the reference model PPR78. Experimental data from our database.*



Main results

The regression procedure of the α-function, simultaneously with the volume translation parameter with respect to the regressed experimental data has been extensively discussed and a general methodology has been proposed [1], leading to the tc-PR model for pure compounds [2]. A database of experimental data for non-associated, associated, ideal and non-ideal binary systems has been developed. It is currently used for the evaluations of the *PPR78* cubic equation of state capabilities [3]. The final step in this work will be the selection of the best mixing rule to incorporate in the *tc-PR* model for mixtures in order to outperform the *PPR78* model.

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2018

Kinetic influence of H_2S on aromatic hydrocarbons pyrolysis at reservoir pressures (700 bar): Experimental study of n-butylbenzene – H2S system compared to pur n-butylbenzene

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

General context, scientific issues

To supply the growing energy demand associated to the increase in population and technological development, oil exploration has moved to unconventional sources like heavy oils found at high temperature and high pressure reservoirs, most of them associated with H_2S and sulfur compounds.

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

After extraction and refining, Oil & Gas companies face the challenging treatment of H_2S 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

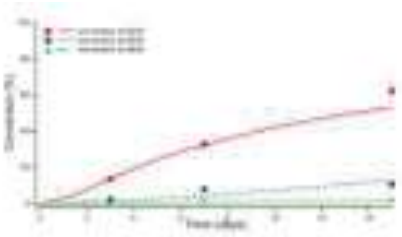
- Understanding the chemistry of sulfur in mixture with hydrocarbons in geological conditions and its effect on crude oil composition.
- Modelling hydrocarbons reactivity in sulfured oil reservoirs.
- Completing and extrapolating the previous studies about oil pyrolysis under geological conditions including the role of H_2S.
- Envisaging the injection of H_2S into depleted oil reservoir as a strategy of environmental treatment of acid gases produced during extraction and refining of hydrocarbons.

Methodology / Experimental approach

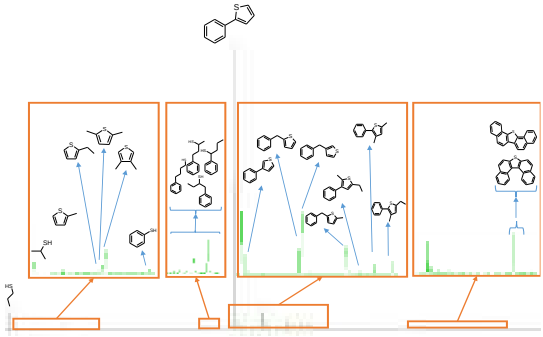
Confined pyrolysis under high pressure (700 bar) and temperature (310°C - 350°C): The sample mixture (n-butylbenzene and H_2S) is introduced and sealed into a gold tube which is heated into an autoclave. The reaction time is set from 3 to 15 days and varies with the temperature to simulate the geological maturation age of the reservoir. The products are identified by GC-MS, quantified by vacuum thermal desorption coupled to a GC-FID and by a GC-FID-FPD system [1, 2, 3]. The results are then compared pure n-butylbenzene pyrolysis performed at the same conditions.

Kinetic modelling: the cracking of n-butylbenzene with and without H_2S is described by a detailed kinetic model based on free-radical chemistry. The model is then validated with experimental pyrolysis data.

Illustration:



Experimental n-butylbenzene conversion (dots, squares and triangles) compared to conversion predicted by the kinetic model at pyrolysis conditions (310°C 330°C and 350°C°)



GC-FPD analysis of n-Butylbenzene-H_2S pyrolysis (350°C, 700bar, 15 jours).

Main results

n-Butylbenzene pyrolysis confirm the high stability of the aromatic cycle to thermal cracking at mild temperature conditions [3].

Main reaction products of n-butylbenzene with and without pyrolysis are shorter alkyl-benzenes (toluene, ethylbenzene and branched butyl benzene) and heptylbenzene isomers.

H_2S accelerates n-butylbenzene cracking at pyrolysis conditions.

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

Inhibition effect of H_2S on alkylaromatics cracking at geological conditions seems to be less significant when compared to alkanes cracking.

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2018	Analytical development on biomass samples Hélène LICHERE (Research Engineer) Anthony DUFOUR Axe CiTherE | GREENER	

Keywords:

Analysis, biomass, wood, lignin, method development, ICP-AES, ICP-MS

General context, scientific issues

Many pilot plants for biomass valorization are currently under development in LRGP. Analysis of the initial biomass (such as wood or lignin samples) and the resulting process products, is one of the most appropriate option to know how efficient the process is in terms of biomass conversion.

Objectives and stakes

In partnership with LERMAB laboratory, the aim of this work is to reduce costs invested in analytical services by taking advantage of the large analytical equipment parks available in LRGP and LERMAB. Developing analytical methods in the lab is time saving and increase the reliability of the results, thanks to our experience in understanding biomass chemistry.

Methodology / Experimental approach

My first mission was to develop an elemental analyzer method for wood samples (analysis of Nitrogen, Carbon, Hydrogen and Oxygen). I had to study the existing ISO standards used in analytical services laboratories, in order to deduce a similar methodology applicable to our equipment. Using wood standards, I improved the protocol and deduced a reliable and repeatable method on our device and wood matrix.

In the same way, I have to determine the best analysis parameters to develop different ICP-AES methods. For example, the analysis of 16 elements on wood samples, or in coal samples (with use of Hydrofluoric Acid). I also work on ICP-MS if I need to analyze element traces.

I always have to evaluate the analysis cost in order to check if it is more interesting to carry out the developed method routinely in the laboratory, rather than send it to an analysis laboratory.

HPLC analyses are also in development on Pectins and Hemicelluloses, using saponification as sample preparation.

Illustration: ICP-AES, Thermo Scientific, iCAP 6300 series

Main results

For wood samples, methods were developed on elemental analyzer (CHN/O), ICP-AES and ICP-MS. I also developed a Sulphur and Chloride analysis by Ion Chromatography, but it was considered too expensive and time-consuming.

Different ICP-AES and ICP-MS methods were developed such as the analysis of Copper, Nickel and Iron in soaked lignins, and Phosphorus analysis in Phosphorus-grafted fibers (designed to make them non-flammable).

HPLC analyses of Furfural, HMF, Acetic Acid, Levulinic Acid, and Formic Acid are now used routinely on Pectins and Hemicelluloses.

References

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2018

Kinetic modelling of the high temperature combustion of a Ramjet Fuel

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Axe CiTherE | GCR

Keywords: Ramjet, fuel, Pyrolysis, Combustion, Reaction Kinetics, Modelling, Simulation

General context, scientific issues

In partnership with the MBDA group, we are conducting research in the field of chemical kinetics to develop a detailed reaction mechanism for the combustion of a ramjet fuel. From the generated mechanism, simulations will be performed using Chemkin Pro (or Cantera) software and will be compared to experimental results available in the literature to validate the model. In a second phase, this validated mechanism will be used to predict the combustion of the fuel under operating conditions close to those used by MBDA.

Objectives and stakes

- Evaluation of physical and chemical properties of a Ramjet Fuel.
- Development of a detailed kinetic model for the high temperature combustion of the Fuel.
- Simulation using experimental data to validate the model.

Methodology

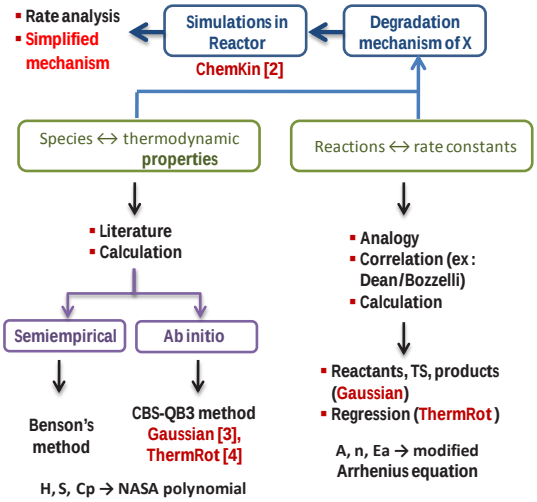
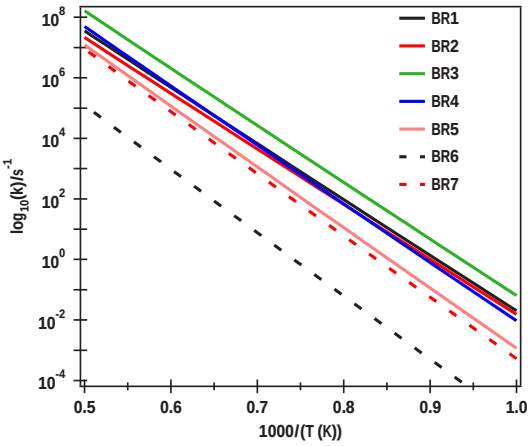


Illustration: Rate coefficients as a function of temperature of the initiation reactions of the Ramjet Fuel



Main results

This work has just started.

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2018

Prediction of thermokinetic parameters for liquid-phase oxidation from an equation of state based on the Statistical Associating Fluid Theory

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

General context, scientific issues

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

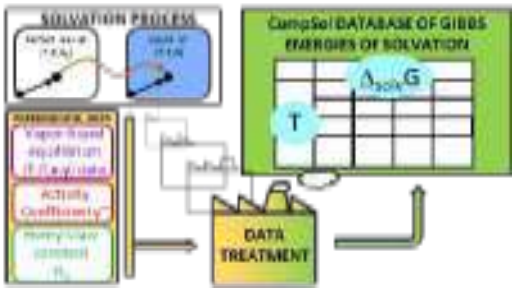
Objectives and stakes

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

Methodology / Experimental approach

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

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



Main results

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

- The number of pure-component solvation energy data was multiplied by 20.
- The number of binary systems was multiplied by 5.
- For each system, the *CompSol* databank contains Gibbs energy of solvation data at different temperatures.
- The CompSol databank contains also entropies and enthalpies of solvation.
- Based on all these experimental Gibbs energy of solvation data in binary mixtures, a link can be clearly highlighted between the solvation process (the fact that a solute will be well or poorly solvated by a solvent) and association phenomena (i.e., interaction between a solute and a solvent through hydrogen bounding).
- A robust PC-SAFT EoS was developed to well represent different thermodynamic properties (containing GIBBS energies of solvation) for pure component. This EoS was compared to cubic-type EoS.

Perspectives

- Prediction of constant rates of complex systems in which liquid oxidation reactions take place using the developed PC-SAFT Equation of State

References

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2018

Experimental study of pollutants formation during the combustion of model molecules from bio-oil

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Keywords: bio-oil, pollutants, combustion, kinetic study, jet-stirred reactor

General context, scientific issues

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

Objectives and stakes

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

Methodology / Experimental approach

The composition of a bio-oil can be very variable considering some parameters. They are: biomass origin, pyrolysis temperature, age of the oil... A very large spectrum of molecules can therefore be found in the bio-oil, that's why a classification by functional group was made. The strategy consists in selecting model molecules which own the same functional group as molecules presents in the oil.

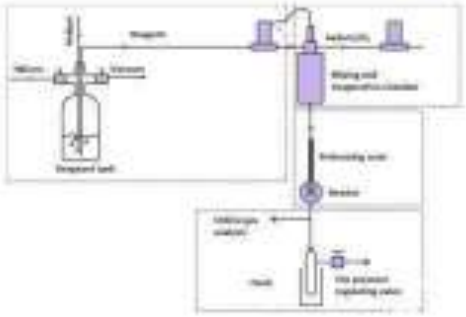
Oxidation experiments were performed using a jet-stirred reactor. Thanks to its both homogeneity in temperature and concentration, it can be considered as an ideal reactor for kinetic studies.

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

Experiments were already carried on 1-pentanol, 1-butanol, butanal, pentanal, butanoic acid and pentanoic acid. Next fuels to be studied are aromatic compounds.

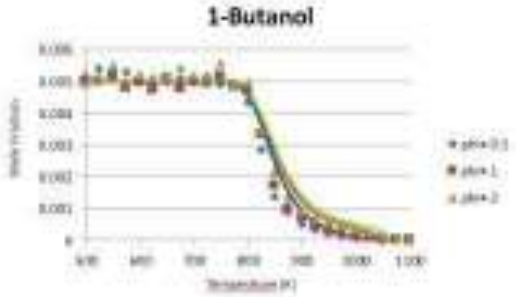
It is also planned to study nitrogen containing fuels with special care taken to the formation of pollutants such as nitrogen oxides.

Illustration: Diagram of the apparatus used for the study



Main results

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



Mole fraction of 1-butanol during oxidation
(x_{fuel}= 0.005, P = 800 Torr, τ = 2s, φ = 0.5, 1 & 2)
Dots represent the experimental data and lines are the simulated data.

References

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2018

Modeling and numerical simulation of LNG behavior in a cryogenic tank

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Keywords: Keywords: Liquefied Natural Gas (LNG), Natural Gas (NG), LNG carrier, Boil-off gas, Thermodynamic, Mass transfer, Thermal transfers, evaporation

General context, scientific issues

The energy and climate challenges of our society impose the need to find alternative and clean solutions.

It is indeed essential to put in place a new form of energy to meet the strong global demand while mitigating the emissions of carbon dioxide and pollutants. In this context, natural gas (NG) is considered a good compromise to ensure an efficient energy transition. It would enable fossil fuel based industries and economies to migrate to cleaner energy solutions such as renewables.

Objectives and stakes

The physical properties of natural gas requires its storage and transportation at high pressures and / or very low temperatures.

Its transport by sea at very low temperatures (-161 ° C) is a major challenge for the industry.

During shipping, Liquefied Natural Gas evaporates due to heat ingress through the tank and sloshing of the liquid. This evaporation is a loss. To reduce these losses, it is essential to understand the behavior of LNG. The objective of the thesis is to understand the main mechanisms responsible for the evaporation of LNG: thermal insulation default, thermal and compositional gradients, thermodynamic behavior of LNG during transport, composition evolution, aging, sloshing of the liquid in the tank etc.

Methodology / Experimental approach

In this thesis, we try to model the thermal and thermodynamic evolution within the tank to predict the behavior of the system and its environment over time.

To do this, a dynamic model (0D) for evaluating heat transfer and thermodynamic properties in LNG transport tanks was developed. The model will be used to study the variation in the quantity, composition and thermodynamic properties of LNG and BOG (Boil-Off Gas) during a typical LNG carrier trip.

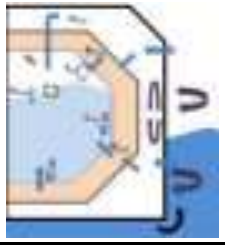
This thesis can be divided in three different steps:

a. Static modeling for the thermal contribution

b. Development of operational BOR concept to estimate real losses by evaporation during the trip

c. Implementation of an optimization strategy

Illustration: Overview of the tank with different physical phenomena



Main results

- The state of the art on the research topic has been finalized. His analysis allowed us to see that most of the studies carried out on the behavior of a LNG tank in operations focused on the aging of LNG by assuming the constant evaporation rate calculated via BOR Design.

It is also found that in most studies, the hypothesis of thermodynamic equilibrium between the liquid phase and the gas phase is considered. This hypothesis is of course very conservative because in reality, the liquid and vapor phase are rarely in thermodynamic equilibrium in the cryogenic storage tanks.

- The evaporation model used is the Hertz-Knudsen correlation. It allows the evaporation of LNG at the free surface of the liquid of a bi-phasic system (liquid-vapor) out of thermodynamic equilibrium

$$\dot{m}_{bog} = \alpha\, S_{interface} \sqrt{\frac{M_{lng}}{2\pi R T_{lng}}} \left(P_{sat}(T_{lng}) - P_{ng}\right)$$

- The coefficient α is called accommodation coefficient.

Its value is between 0 and 1. This coefficient is determined experimentally by the minimization method between simulation and measurement.

$$Erreur_{BOG}(\alpha) = \sum_{i=1}^{N} \left(BOG_{measured} - BOG_{simulated}(\alpha)\right)^2$$

$$\frac{dError_{BOG}(\alpha)}{d\alpha} = 0$$

Perspectives

- Implementation of optimization strategy

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2018

Pyrolysis in pressurized swept fixed bed reactor

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Keywords: slow pyrolysis; pressure; swept fixed bed reactor, secondary pyrolysis reaction, char properties

General context, scientific issues

The effect of pressure during pyrolysis is still yet not really well understood. Some studies[1-2] have shown that the absolute pressure had a negligible effect (or even negative) on the charcoal yield, contrary to other studies[3-5] that reported an increase in charcoal yields and incondensable gases at the expense of tars. Clarifying the effect of the pressure on the products of the pyrolysis remains important since Cetin et al.[6] showed that the pressure would tend to modify the structure and the morphology of the obtained char and thus influence its properties (adsorption) and reactivity (secondary reactions, oxidation).

Illustration:

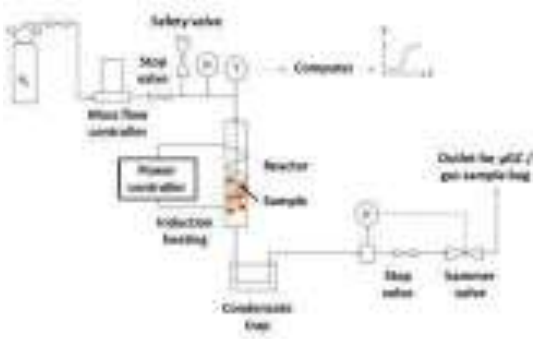

Fig 1 : Schematic diagram of the experimental system

Objectives and stakes

Our objective is to study experimentally in pressurized swept fixed bed reactor the contribution of the absolute pressure on the pyrolysis products by taking into account the parameters which can also act on the residence time of the pyrolysis vapors in the reactor that are the gas flow rate and bed density.

Methodology / Experimental approach

Our strategy is based on a good control of the thermal history of the wood particles. Indeed, for each absolute pressure imposed, the flow rate of the inert gas is corrected so that the partial pressure of the gases formed is always the same. Experiments are carried out in a reactor presented in fig 1 that can operate at a maximum pressure of 10 bars. All products obtained (char, gases and condensed liquid phases) will be analyzed.

To better understand and explain the effect of studied parameters, our methodology will be based on a multi-criteria analysis of the obtained products, i.e. char composition, structure (degree of aromaticity, DRX) and morphology (porosity, surface area, SEM) but also composition of condensable vapors (phenol, polyphenol, etc.) and pyrolysis gases.

Main results

We hope to:

- determine the effect of absolute pressure, partial pressure and bed density on pyrolysis product yields;
- understand their interactions on pyrolysis side reactions and formation of secondary char;
- improve pyrolysis modeling by formulating hypothesis on secondary reactions mechanisms in pressurized pyrolysis.

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2018

A product-design approach for an optimization of the working fluid in the cycles of thermal and refrigeration machines of tomorrow

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Keywords: Product Design, Thermodynamic Cycles, Power Generation, Refrigeration, Computer-Aided Molecular Design

General context, scientific issues

Ozone depletion and global warming are two major environmental concerns for the future development of the power generation systems and refrigeration-based industries. Aiming at dealing with these two problems, since mid-1980s, a series of international treaties have been established. The Montreal Protocol (1987) demanded a gradual phase out of CFCs. In 1997, Kyoto Protocol imposed that most countries had to reduce GHG emissions. Recently, the F-gas Regulation (2014) established the Global Warming Potential (GWP) limits to most of the refrigeration and air conditioning vapor compression systems. Finally, policymakers have been focused on the 2°C decrease scenario, which aims at limiting average global temperature increase to 2°C [1], [2].

In order to respect environmental treaties, the computer-aided molecular design (CAMD) arises as a promising technique to determine new suitable working fluids for cycles used in power generation and refrigeration systems.

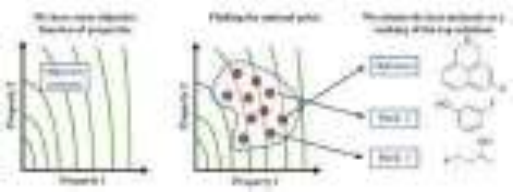
Objectives and stakes

The objective of this thesis is the development of a methodology of research – based on computer-aided molecular design techniques - for an optimal working fluid, energetically performing and respecting the current environmental standards, for cycles of thermal and refrigeration machines.

Methodology / Experimental approach

The first stage of the project will be focused on the development of thermodynamic models in order to be able to guess saturation and energetic properties of different pure-compounds and binary mixtures. Secondly, a simulation tool, based on appropriate computer-aided molecular design, will be built in order to assess the performance of considered working fluids during cycle optimizations. With this tool it will be possible to identify the expected properties of use, to connect them with the physico-chemical properties and to propose a strategy of choice by connecting thermodynamic models and multi-criteria analysis tools.

Illustration: Pictorial representation of the problem of finding an optimal molecule [3].



Main results

A literature review on the evolution of environmental policies has been conducted as well as on the identification of the most used cycles for power generation from: (1) high-temperature heat sources – Hirn cycle, Brayton cycle, Diesel cycle - and (2) medium- and low-temperature heat sources – Organic Rankine cycle, Kalina cycle – such as waste heat and renewable energy sources. Furthermore, a literature review on the technologies used in refrigeration industry and the working fluids that are contained in installed machines, has been completed.

In order to determine the properties of working fluids, a study on the cubic equations of state has been just finished. The main objective was to determine which properties among vapor pressure, enthalpies of vaporization and saturated liquid heat capacities were suitable to perform fitting of α-function parameters coupled with the Peng-Robinson and the Redlich-Kwong EoS. It was determined that safe parameters were obtained when fittings were conducted taking into account at least vapor pressure data.

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2018

Experimental study of the formation of NOx during the combustion of biogas

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Axe CiTherE | GCR

Keywords: biogas ; oxidation ; NO_x ; jet stirred reactor

General context, scientific issues

In September 2016, the IMPROOF project started. This project is funded by the European Union and brings together 11 partners from 6 different countries, including the LRGP from Nancy. The aim is to improve the energy efficiency of steam cracking furnaces by an economical optimization and a reduction of pollutant emissions. For this purpose, laboratory studies and industrial pilots are carried out in order to improve the designs and materials of the furnaces. In parallel, modelling will be developed on these furnaces as well as the study of alternative fuels, especially those derived from biomass [1-2].

Objectives and stakes

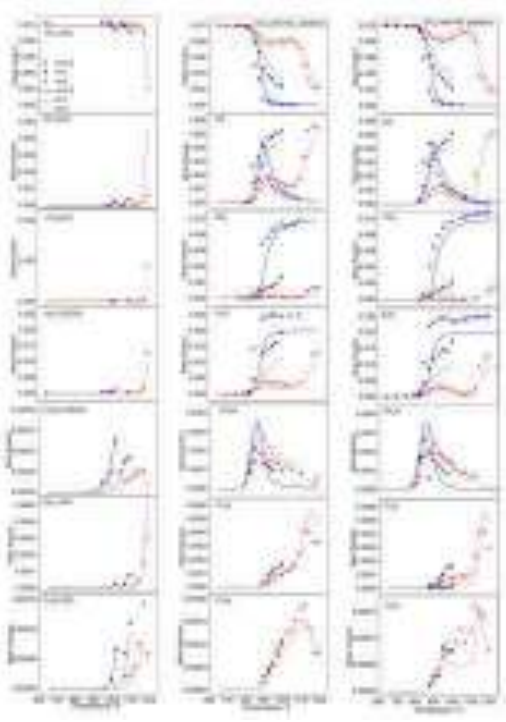
To investigate the influence of the addition of NO on combustion of biogas surrogates in an O_2/inert gas mixture at moderate temperatures in a quartz jet-stirred reactor.

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

Methodology / Experimental approach

The experimental setup was a laboratory-scale spherical fused silica JSR (volume of 85 cm3). The reactant gases were premixed in a preheating zone before entering the reactor center. The residence time in the reactor was fixed at 1.5 s within all the experiments investigated. The reactor was heated using Thermocoax resistances. The reactor temperature was measured by a type-K thermocouple located at the center of the reactor. The pressure in the reactor was controlled by a needle valve positioned downstream of the reactor and kept at 107 kPa. Argon, oxygen, NO, NO2 and methane were provided by Messer (purities of 99.99%, respectively). The flow rates of the reactants were controlled by mass flow controllers. The gases leaving the reactor were analyzed on-line using two gas chromatographs (GCs), a NOx analyzer (Thermo Scientific Model 42i), a FTIR (Thermo Scientific Antaris) spectrometer and a cw-CRDS spectroscopy cell.

Illustration: Species profiles comparison between experimental data and model predictions are shown in below. The left column is for the oxidation of neat methane; the middle column is for the oxidation of methane doped with NO_2 (400 ppm); the right column is for the oxidation of methane doped with NO (500 ppm).



Main results

The agreement between the experimental data and simulated results is generally very satisfactory within all the investigated conditions except for the model underestimation of the experimental profile of H_2O under stoichiometric and fuel-lean conditions. The effects of NO and NO_2 on CH_4 oxidation are very close.

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2018

Kinetic study of the gas phase pyrolysis of organic molecules containing heteroatoms. Application to the optimization of a soil remediation process by vacuum pyrolysis.

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Keywords: Soil remediation, pyrolysis, organic molecules, kinetic study, jet stirred and tubular reactor.

General context, scientific issues

Soil remediation becomes more and more important for the preservation of the environment and human health and the reuse of polluted areas. Several strategies can be used according to the nature of organic pollutants. Thermal desorption followed by thermal decomposition can be used for the treatment of pollutants such as hydrocarbon fuels, poly-aromatic hydrocarbons, or species containing heteroatoms (e.g. chorine, sulphur).

Objectives and stakes

The objective is to study the pyrolysis of molecules with similar structure to pollutants. It is crucial to understand the chemistry of thermal decomposition of these pollutants to predict the influence of operating conditions on the nature and concentration of reaction products.

Methodology / Experimental approach

Two different reactors are used for this study: a jet-stirred-reactor (JSR) and a tubular reactor (TR, assimilated to a Plug Flow Reactor under our conditions). Experiments in JSR were performed at a constant pressure of 1.067 bar (800 torr), at a residence time of 2 seconds and at temperatures ranging from 800 to 1150 K.
Experiments in the TR were performed at a constant pressure of 1.067 bar, at a residence time in the set-point temperature zone around 2 seconds and at temperatures ranging from 800 to 1300 K.

The inlet gas leaving the reactors was analyzed using two gas chromatographs and a Fourier Transform InfraRed spectroscopy (FTIR) analyser via a heated transfer line maintained at 433 K to avoid product condensation.

Illustration:

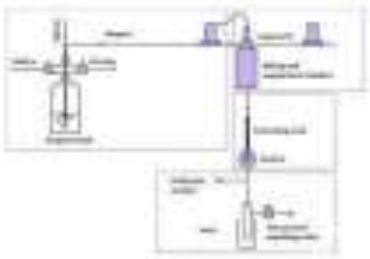


Diagram of the apparatus used for the pyrolysis study

Main results

The pyrolysis of bromoethane has been studied in the jet stirred reactor. Chlorobenzene, nitromethane and diethylamine have been studied in a tubular reactor.

The pyrolysis of bromoethane is controlled by an unimolecular reaction: Bromoethane is converted into hydrogen bromide and ethylene which are the main products. The molecule is completely consumed at 973 K (800 torr, 2s, molar fraction of 0.01).

Chlorobenzene was nearly fully destroyed in the TR (95% of conversion) for an experiment at 800 torr, a residence time of 2 seconds and an inlet mole fraction of 0.005 at a temperature of 1250 K. The use of a tubular reactor inhibits the formation of aromatic products like biphenyl, biphenylene, chlorobiphenyls and dichlorobiphenyls.

The Pyrolysis of nitromethane leads to a large formation of nitric oxide, carbon monoxide, methane and formaldehyde. The molecule is fully destroyed at 825 K (800 torr, 2s, molar fraction of 0.01). Traces of NO_2, acetonitrile and hydrogen cyanide are observed.

The Pyrolysis of diethylamine is more complex. It is leading to the formation of a lot of species. Methane, ethylene, ethane, hydrogen cyanide and acetonitrile are major products. The molecule is fully destroyed at 950 K (800 torr, 2s, molar fraction of 0.01).

2018

Modeling of the spray process for natural gas transport tanks

Xiaochun XU (Research Engineer)

Jean-Noël JAUBERT, Romain PRIVAT
Axe CiTherE | ThermE

Keywords: Liquefied Natural Gas, spraying process, modeling, Equation of State

General context, scientific issues

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

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

Scheme 1. the spraying process of LNG

Objectives and stakes

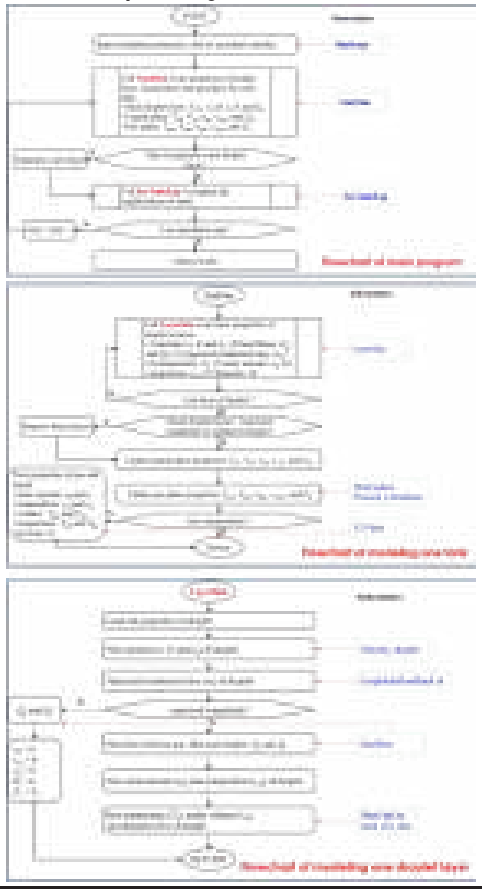
In this work, the previous developed simulation program of the spraying process in one tank is further extended to the process including several connected LNG tanks, and the evolution of LNG properties is also considered now.

Methodology / Experimental approach

Equilibration of two tanks:

Evolution of LNG properties:

Illustration: Proposed algorithm



Main results

(1) The spraying simulation program is extended to the processes including several connected LNG tanks. The pressure equilibrations between tanks are considered.
(2) The evolution of LNG properties during the spraying is implemented in current program.

References

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2018

Effect of celluloses structure on fast yrolysis products in micro-fluidized bed reactor

Yanan ZHU (3rd year)

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Keywords: cellulose, allomorph type, degree of crystallinity, fast pyrolysis, micro-fluidized bed

General context, scientific issues

Cellulose is a major chemical constituent of lignocellulosic biomasses which are expected renewable resources for fuels, materials and chemicals. Fast pyrolysis process can give a maximum yield of organic liquids from biomass materials. Fast pyrolysis of cellulose is useful for the production of sugars, especially for levoglucosan. So far, we do not know yet well effect of cellulose structure on pyrolysis products, notably on sugars.[1]

Objectives and stakes

This work aims at investigating effect of cellulose structure on pyrolysis products during fast pyrolysis, especially on sugars, realizing the qualitative and quantitative analysis of main pyrolysis products as well as the intermediate products during agglomeration, and developing the pyrolysis mechanism of celluloses with different structures.

Methodology / Experimental approach

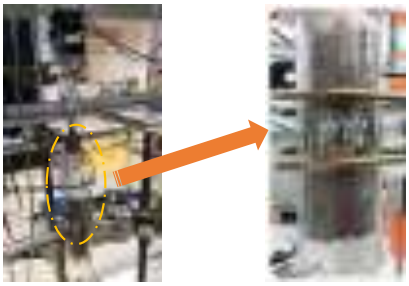
Cellulose analysis: Degree of crystallinity of cellulose was detected by X-ray diffraction(XRD). The number-average molecular weight(Mn) and weight-average molecular weight(Mw) were determined by Gel permeation chromatography (GPC). Micro-structure of cellulose and the obtained char were detected by scanning electron microscope (SEM). Metal elemental analysis was realized by Inductively coupled plasma mass spectrometry (ICP-MS) analysis.

Pyrolysis of cellulose: Pyrolysis of cellulose at different experimental conditions was performed by using micro-fluidized bed[2], which combined with continuous injection setup.

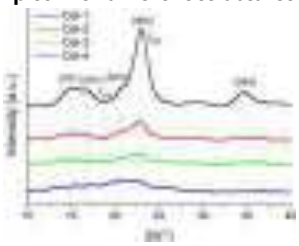
Analysis of pyrolysis products: Analysis of bio-oil and intermediate liquid using GC/MS-FID and HPLC-SEC-ELSD-MS.

Illustration:

Micro-fluidized bed reactor combined with continuous injection setup.



Cellulose samples with different structures



Main results

Micro-fluidized bed reactor combined with continuous injection setup has been developed and the pyrolysis conditions have been optimized. It can realize the good fast pyrolysis of cellulose. The yield of levoglucosan has reached to 20% of the weight of cellulose feed. After treatment, cellulose samples show different structures with different degrees of crystallinity and different DP values. The yield of the main pyrolysis products are different.[1]

Next, the intermediate products of agglomeration during fast pyrolysis will be quenched and analyzed. Qualitative and quantitative of main products will be realized and the pyrolysis mechanism will be developed.

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PRODUCT ENGINEERING

LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

2018

Hydrogen production using heterostructuredphotocatalystsassociating perovskite and carbon nitride

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Raphaël SCHNEIDER, Thomas GRIES (IJL)
Axe Product Engineering | EMMAD

Keywords: Perovskite, Nanomaterials, Solvothermal synthesis, Hydrogen production, Photocatalysis.

General context, scientific issues

In recent years, the production of hydrogen by photochemical decomposition of water has received a lot of attention because it is one the most promising methods in terms of cost and environmental impact. In this context, we propose to develop photocatalytically active iron-based perovskites ($SmFeO_3$) associated with graphitic materials to achieve good solar energy conversion efficiencies for H_2 production.

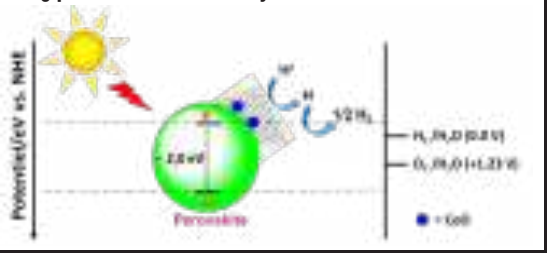
Objectives and stakes

The objective of this work is to synthesize the Fe-based perovskite$SmFeO_3$. $SmFeO_3$ will be associated with graphitic carbon nitride C_3N_4 that will promote an optimal delocalization of photogenerated electrons and thus increase their ability to reduce water.
In a second step, the introduction of co-catalysts like NiS or CoOon the surface of$SmFeO_3/C_3N_4$composites will also be evaluated. These co-catalysts are also intended to facilitate the separation of charge carriers and thus allow an improvement in the efficiency of H_2photoproduction.

Methodology / Experimentalapproach

To achieve the objectives previously described, the following methodology will be implemented:
1- Synthesis and characterization of graphitic materials.
2- Synthesis and characterizations of SmFeO3 particles.
3- Preparation of heterostructured catalysts associatingSmFeO3 and C3N4.
4- Evaluation of the catalyst performance forthe photodegradation of organic pollutants.
5- Evaluation of the catalysts performance to photogenerateH2.
6- CoOor NiS nanoparticles used as co-catalyst will be deposited on the surface of SmFeO3/C3N4 photocatalystsdepending on the performance achieved in H2 production.

Illustration: Principle of photoproduction of hydrogen using perovskite/C_3N_4 catalysts



Main results

•$SmFeO_3$particles were successfullyprepared by a solvothermal route followed by calcination at 600 °C for 2 h. These particles were associated to $C_3N_4$by ultrasonication for 90 min followed by drying.
•The crystal structure and phase purity of the neat and nanocompositephotocatalysts were analyzed via X-ray powder diffraction(XRD). The results revealed thatpure $SmFeO_3$ particlesin an orthorhombic crystal phase (JCPDS n° 74-1474)were prepared [1, 2].
•Transmission electron microscopy (TEM) images showthat $SmFeO_3$particles exhibit a quasi-spherical morphology and an average size of 22.5 nm.
•The optimal photocatalytic activity was observed using a weight ratio $SmFeO_3/C_3N_4$ of 20/80.
•$SmFeO_3/C_3N_4$photocatalysts can be used under visible light irradiation to degrade persistent pollutants in aqueous effluents.

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2018

Design and development of a hydrometallurgical process of Cobalt (II) recovery from secondary mining by precipitation

Neïla DJOUDI (1st year)

Hervé MUHR, Marie Le Page Mostefa
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Keywords: Precipitation, Hydrometallurgy, Cobalt, Purification, Metal recovery

General context, scientific issues

Critical metals, such as cobalt, are particularly strategic because they are present in many high added value products. Besides, at the rate of current consumption of these metals and more particularly cobalt, the manufacturers are facing risks of shortage for their supply. Therefore, research on the recovery of these metals, from industrial or urban waste, are important for the coming years.

The low concentration of metals contained in leachates is one of the main difficulty for their recovery. This is why the recovery and the separation of metals remain complex and require new developments for their purification. Thus, attention has been focused on precipitation, which is a first-order separation process in the field of hydrometallurgy [1].

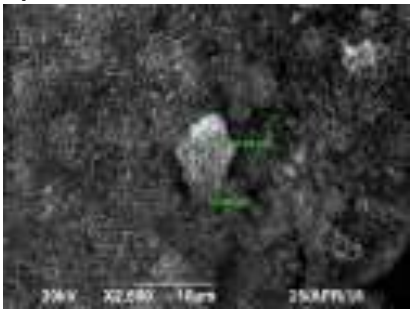
Objectives and stakes

Leachate contains a mixture of many metals such as copper, manganese , nickel and cobalt . The aim of this work is to develop a hydrometallurgical process to recover cobalt from leachates by precipitation .

Methodology / Experimental approach

In a first step, precipitation of cobalt hydroxide will be investigated in a synthetic solution containing only Co(II). Several operating parameters will be varied during the experiment, in order to identify the best condition for a recovery higher than 99%, a good filtrability and kinetic of precipitation of cobalt hydroxide will also be determined.
In a second step, precipitation of cobalt hydroxide will be investigated in a complex synthetic media including a set of metal cations, as well as the actual leaching solutions of secondary mines. Experiments will be conducted in a stirred tank reactor (1L) at 25°C and then in a reactor with a high solid density.

Illustration: SEM image of crystalline cobalt hydroxide α-$Co(OH)_2$



Main results

-Bibliographic research on the precipitation agent of Cobalt (II) has been done (easily filterable, selective, highly insoluble...)
- Simulation of cobalt precipitation with different anions (carbonate, hydroxide, sulphide, oxalate), with Phreeqc and visual Minteq has been done. This simulation makes it possible to compare the efficiency of precipitation with this different precipitant, by indicating the saturation indices, the residual concentrations of the different species as well as the precipitation rate.

- Experiments with hydroxide cobalt precipitation have been conducted by varying different parameters.

- The optimization of the operating parameters of the process should allow a better control of the granulometry of the precipitate and reactors with high solid density will be implemented. Other precipitating agents (sulfide, oxalate, phosphate) will also be considered.

References

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2018

Composites of Polystyrene with Cross-Linked Particles and Study of the Kinetics of Free Radial Polymerization of Styrene in a 3D Network: an Application for Used Tire Rubber Recycling

Daniela FLOREZ (3rd year)

Guo-Hua HU, Dimitrios MEIMAROGLOU

Axe Product Engineering | GP2

Keywords: Used tires recycling, polystyrene, free radical graft polymerization, polymer composites.

General context, scientific issues

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

Nowadays, waste tire rubber is ground to obtain small granules called GTR, which present a cross-linked molecular structure and are blended with polymers to make high value-added materials. This idea is not only a promising strategy and economical method for reusing tire rubber, but also a solution for production of low-cost composites [1]-[2].

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

Objectives and stakes

This research project aims to develop a PS composite by addition of rubber granulates from used tires recycling in order to obtain a product which can be advantageously reused.

Methodology / Experimental approach

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

Illustration: *Styrene graft-polymerization in presence of GTR particles in a batch reactor.*

Main results

Experimental results. Both phases can by effectively compatibilized by grafting the PS chains onto the elastomeric chains present in the GTR particles. Moreover, it was observed that the final monomer conversion and percent of grafted chains are mainly influenced by the rubber content and the temperature of the reaction.

Modelling results. The model was developed (using MATLAB® software) on the basis of the comprehensive kinetic model for the combined chemical and thermal polymerization of styrene. Nevertheless, to better understand the effect of rubber particles on the behavior the system, a thermal study (i.e, DSC) of the kinetics of the polymerization was also performed in parallel. The analysis of the results of this study will help improve the kinetic model towards a more accurate prediction of the polymer properties such as conversion, grafting rate and average molecular weight.

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2018	Mn-doped Ag-In-Zn-S QDs as dual-modality probes for magnetic resonance and fluorescence imaging of cells Perizat GALIYEVA (2nd year) Raphaël SCHNEIDER, Halima ALEM-MARCHAND Axe Product Engineering PPM | EMMAD	

Keywords: ZAIS QDs synthesis, doped QDs, physico-chemical characterization, fluorescence, aqueous phase transfer

General context, scientific issues

Colloidal semiconductor nanoparticles have attracted considerable interest due to their size and composition dependent optical properties originating from (*i*) changes of the surface-to-volume ratio with size and (*ii*) quantum confinement effects. The optical properties of these semiconductor quantum dots (QDs) have been studied for applications in bioimaging, light emitting diodes, solar cells,... (2).

QDs doped with paramagnetic ions are also of high interest due to their potential use in numerous biological applications (bimodal imaging, fluorescence and magnetic resonance imaging (MRI), targeted drug delivery, biodetection, sorting of cells, ...).

Objectives and stakes

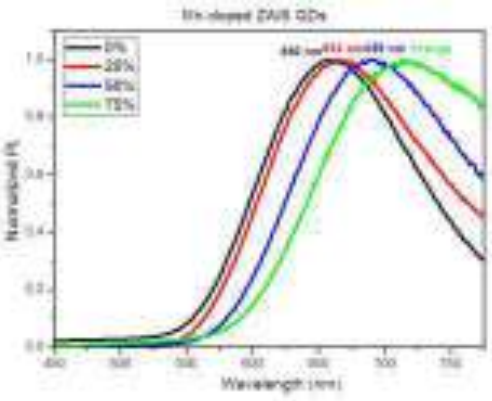
1. One-step synthesis of undoped and Mn-doped Ag-In-Zn-S QDs,
2. Physico-chemical characterization of organic phase synthesized QDs,
3. Aqueous phase transfer of hydrophobic ZAIS QDs.

Methodology / Experimental approach

QDs with different photoluminescence (PL) emissions were synthesized in the 1-octadecene organic solvent and using dodecanethiol (DDT) as capping ligand. The synthesis was carried out by a one-step method (for the doped nanoparticles, the dopant was introduced together with all precursors).

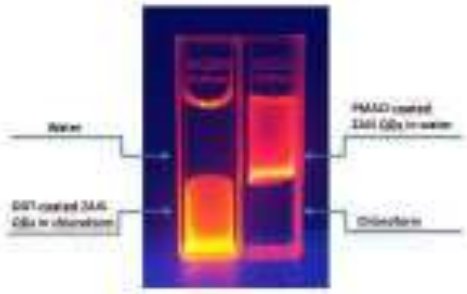
The PL emission of the product was controlled by the value of x in the (AgIn)xZn2(1-x)S2 materials. TEM and XRD demonstrate that the QDs are of spherical shape (average diameter of ca. 5 nm) and with an orthorhombic structure. Hydrophobic DDT-capped QDs were successfully transferred in water by surface modification or ligand exchange. Doping with Mn2+ ions of ZAIS QDs make them paramagnetic. A red-shift of the PL emission after Mn2+ doping.

Illustration: Photoluminescence spectra of undoped and 25%, 50%, 75% Mn-doped ZAIS nanocrystals



Main results

1. Mn-doped (25%, 50% and 75%) Ag-In-Zn-S and undoped Ag-In-Zn-S QDs were prepared using a one-step synthetic method in organic medium;
2. Physico-chemical properties of synthesized QDs have been studied;
3. Synthesized ZAIS QDs were successfully transferred to aqueous phase by surface modification with poly (maleic anhydride-alt-1-octadecene) (PMAO).



Phase transfer of DDT-coated ZAIS QDs using PMAO

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2018

Hydrogen photoproduction by water splitting using $LaFeO_3$ associated to carbon nitride

Vincent GUIGOZ

Raphaël SCHNEIDER, Thomas GRIES (IJL)
Axe Product Engineering | EMMAD

Keywords: Hydrogen, water splitting, perovskite, $LaFeO_3$, carbon nitride

General context, scientific issues

In the endless growing demand for energy, new ways of energy production are needed to counter energy shortage and environmental pollution from non-renewable fossil fuels. Hydrogen is a potential energy source and water splitting allows its production using only water and sunlight. $LaFeO_3$ bandgap allows to use visible light for water splitting and is composed of non-toxic and abundant elements.

Objectives and stakes

Two synthesis methods will be used to produce $LaFeO_3$ and a study will devoted to compare advantages and drawbacks of each one. These two methods are suited for large scale production, making it available for industries. To improve the efficiency, different heterojunctions will be made, still using non-toxic elements. A full study devoted to the use of $LaFeO_3$ for new energy production and how to make it at a large scale will be conducted.

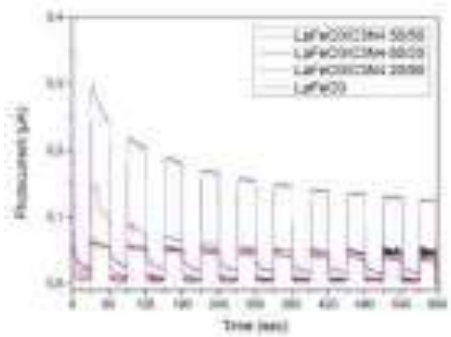
Methodology / Experimental approach

This project is developed between LRGP and Institut Jean Lamour (IJL). At LRGP, a chemical synthesis is performed by a solvothermal process in order to produce nanopowders. At IJL, LaFeO3 is synthesised by a plasma process using Physical Vapor Deposition (PVD) to create thin films directly deposited on a substrate. At LRGP, heterojunction with g-C3N4, a 2D graphene-like material, was already prepared to determine its effect on photocurrent and photocatalytic efficiency. At IJL, we needed to find parameters for deposition and for annealing to obtain crystallisation with good stoichiometry.

Next, the effect of LaFeO3 film thickness on photocurrent efficiency will be investigated.

To study hydrogen production, two different methods will also be used. At LRGP, hydrogen will be produced in a tight cell where hydrogen will be sampled at regular intervals by Gas Chromatography. At IJL, hydrogen will be measured by Mass Spectroscopy, allowing more continuous measurements.

Figure : Photocurrents measurements of $LaFeO_3$/g-C_3N_4 heterojunctions



Main results

Thanks to Bilel Chouchene's work, solvothermal parameters for $LaFeO_3$ synthesis were defined. We could directly start working with g-C_3N_4 heterojunction. In the literature, we found two articles with opposite conclusions. The first one demonstrates that a high percentage of $LaFeO_3$ gives a better photocurrent [1], while the second one indicating that a smaller percentage of $LaFeO_3$ vs g-C_3N_4 is preferable [2]. Based on these results, we decided to study three heterojunctions: $LaFeO_3$/g-C_3N_4 80/20, 50/50 and 20/80.

Using photocatalysis and photocurrent measurements, better results were obtained with the $LaFeO_3$/g-C_3N_4 20/80 material (see Figure).

At IJL, we had to correct parameters to deposit La and Fe on a substrate in equal stoichiometry. Then, we also had to find the parameters for the annealing process to obtain a good crystallinity. After that, we measured photocurrent values of different thin films with various thicknesses. We observed that going under 100 nm thickness gives better results, likely due to decreased electron/hole recombinations.

Next step is to obtain high and reliable hydrogen photoproduction with the different samples prepared.

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2018

Evaluating Thermoplastic Compounded with Tannin and Tannin-based Resin by dynamic extrusion process

Jingjing LIAO (3rd year)

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Axe Product Engineering | GP2

Keywords: Tannin-based resin, polypropylene, dynamic extrusion, tannin modification, poly(lactic acid), 3D printing filament

General context, scientific issues

Tannin is one of the most abundant polyphenols, widely distributed in vascular plants and soft tissues of woody plants. A growing attention has been given to tannin due to their reactivity; biological activity; high hydroxyl group; and functionality. Those are recognized advantages for developing tannin as a component of plastics. According to literatures and our previous works, the mechanical property and other properties of polyester can be improved by incorporation of tannin resin or tannin. Furthermore, its biological property also interesting on biodegradable plastics. Thus, combined with 3D printing technology provides an effective manufacture and waste minimization way to produce components with complex geometries according to computer designs.

Objectives and stakes

The object of this work is to develop the potential applications of tannin resin and modified tannin on plastic materials, especially on those biodegradable plastics. Furthermore, their utilization as 3D printing materials will be evaluated.

Methodology / Experimental approach

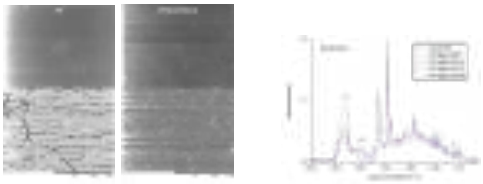
1. tannin acetylation(AT)

Tannin was acetylated with acetic anhydride in weight proportion 1:5 with 5% pyridine as a catalyst. The suspension was precipitated in ice water and centrifuged to separate the solution. Acetylated tannin powder was washed 5 times with distilled water. Air dry for several days.

2. Extrusion process

The Poly(lactic acids)/tannin acetylation(PLA/AT) composites were prepared by an extruder with a screw diameter 11mm and a length-to-diameter ratio L/D=40. The screw profile is presented in figure 1. It is composed of three mixing zones with different configurations of kneading blocks for promoting dispersive and distributive mixing. All compounds were well blended at the certain proportion in a baker before injecting into the extruder. The filament was collected with a spool.

Illustration:



1. the SEM(left) and FTIR spectrum(right) of PP/tannin resin composite after accelerated weathering

2. PLA/AT filament and its printed product

Main results

1. Polypropylene/tannin resin composite

Polypropylene(PP)/tannin resin composite was successfully produced by dynamic extrusion process. The tannin resin was well dispersed into the PP matrix and reinforced it. This composite displays higher Young's modulus compared with neat PP, and better mechanical properties can be found with the addition of 5% MA-g-PP as a compatibilizer. The addition of tannin resin yields a more sensitive linear viscoelastic region to the PP matrix, their complex viscosity (η^*), storage modulus(G') and loss modulus(G'') increasing with increasing tannin resins content except for the 30% tannin resin content case. By increasing tannin resin content, PP/tannin resin composites present an improvement of char yield. Furthermore, tannin resin displays a good weather retardant property.

2. PLA/AT filament

Both tannin and tannin acetylation were successfully compounded with PLA. However, the filament based on PLA/tannin failed to use for 3D printing. The characterization and analysis will be done in the near future.

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2018

Transitional Phase Inversion Emulsification with Surfactant Copolymers

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Cécile NOUVEL, Véronique SADTLER

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Keywords: Transitional Phase inversion, Conductivity, Copolymer surfactant, Emulsification, Phase Inversion Temperature

General context, scientific issues

The nanoemulsions (droplet size from 20 to 200 nm) have many interesting properties: no sedimentation, an optical transparency, a greater stability and above all a greater specific surface area. Unfortunately, their formation traditionally requires high-energy techniques such as high-pressure homogenizer. The Phase Inversion Temperature (PIT) is a promising technique for producing nanoemulsions [1] but its mechanisms remain not fully understood. Moreover, the phenomenon relies heavily on the architecture of the surfactant and only small surfactants have been widely studied until now.

Objectives and stakes

The aim is to optimize emulsification process through PIT with polymer surfactant in the formulation. So far, no large polymeric surfactant was used in the literature to obtain a nanoemulsion thanks to a PIT emulsification. Therefore, we must understand the impact of the polymer structure on the phase inversion mechanism and determine the limitation of polymers to produce efficiently nanoemulsion with a phase inversion temperature technique.

Methodology / Experimental approach

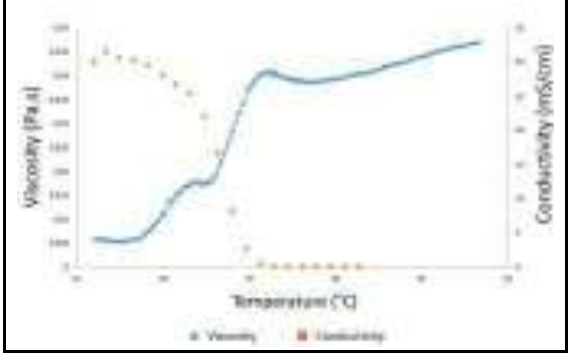
1) Creation of the experimental setup for the phase inversion temperature technique procedure :
- Determination of the parameters for the PIT emulsification using any surfactant available [2][3]
- Testing of commercial polymers as surfactants

2) Design and synthesis of copolymer surfactants for their application in PIT emulsification method

3) Realize nanoemulsions through phase inversion temperature with copolymer surfactants

4) Study the impact of composition and the (co)polymer structure in order to define in details the relation between their composition/structure, their capacity to participate in the phase inversion mechanism and the resulting properties of the nanoemulsions produced.

Illustration: Conductivity and viscosity profiles during a phase inversion temperature procedure



Main results

Several commercial surfactants including an ethylene oxide part have been tested with the same system dodecane-water for a wide range of surfactant concentrations. Commercial products belonging to the Brij family were used as model of low molecular surfactant. In order to investigate high molecular weight surfactants, polystyrene-b-poly(oligo ethylene glycol methacrylate) diblock copolymers (PS-POEGMA) were designed and studied as potential polymeric surfactants for the temperature phase inversion technique.

- The PIT procedure carried out with some Brij as a surfactant lead to nanoemulsions (mean diameter around 95 nm), which were very stable (> 2 months)
- Several commercially available copolymer surfactants (Pluronics) were tested but were ineffective for a PIT emulsification
- PS-POEGMA was synthesized through ATRP in order to control precisely its length and block ratio and it was found to be usable for a PIT procedure

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2018

Quaternary ZAIS quantum dots for optoelectronic applications

Maroua MRAD (1st year)

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Keywords: Core/shell Quantum Dots, AIS and ZAIS, UV-visible absorption, photoluminescence.

General context, scientific issues

In the past few decades, photoluminescent semiconductor quantum dots (QDs) have been extensively investigated due to their numerous potential applications. Indeed, QDs exhibit high photoluminescence (PL) quantum yields along with size and composition dependent PL properties.
Ternary I–III–VI$_2$ QDs, such as $AgInS_2$ (AIS), are of high potential as they contain no highly toxic elements and thus they have been investigated for applications ranging from bioimaging to LEDs [1].
In the present study, new syntheses of AIS and $AgInS_2$/ZnS (ZAIS) QDs were developed in aqueous media and their optical properties were investigated.

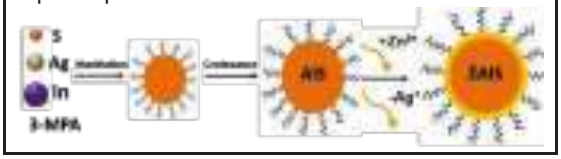
Objectives and stakes

Our objective is the development of aqueous-based syntheses of ternary AIS and quaternary ZAIS QDs. Various synthetic parameters like the molar ratios Ag/In ratio, the capping ligand, the pH of the reaction medium ... were investigated.
The syntheses are combined with spectroscopic analyzes and particularly by measurements of the PL spectra at different stages of nanoparticles growth in order to optimize the optical properties.

Methodology / Experimental approach

AIS QDs were prepared at 100°C by injection of Na_2S into an aqueous solution of $AgNO_3$, $In(NO_3)_2$, and of the capping ligand adjusted at pH 8.
A ZnS shell was installed at the periphery of the AIS core by injection of $Zn(OAc)_2$ (see Figure).
Various ligands such as 3-mercaptopropionic acid (3-MPA), mercaptosuccinic acid, cysteine, N-acetylcysteine were investigated.
The growth of AIS and ZAIS nanocrystals was monitored by UV-visible and PL spectroscopy.
The prepared AIS and ZAIS nanocrystals were characterized by UV-visible absorption and PL spectroscopy. AIS and ZAIS QDs were also characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

Synthetic route used for the preparation ZAIS QDs in aqueous phase



Main results

- The best optical properties for AIS and ZAIS QDs were obtained using 3-mercaptopropionic acid as capping ligand.
- XRD shows that all the peaks of the AIS and ZAIS QDs can be indexed to the tetragonal chalcopyrite $AgInS_2$ phase (JCPDS No. 01-075-0117). After the growth of ZnS at the periphery of the AIS core, the position of the peaks moves towards the standard position of ZnS with a blende structure, which proves the formation of the core/shell structure. This shift also indicates that the diffusion of Zn^{2+} ions into the core results in a change in the network parameters of the $AgInS_2$/ZnS nanocrystals.
- TEM demonstrates that the AIS and ZAIS QDs are of spherical morphology and that their size increases with the silver content from 3.4 nm to 4.8 nm.
- The incorporation of Zn^{2+} into the core and the cation exchange $Ag^+ \rightarrow Zn^{2+}$ strongly influence the optical properties of the QDs.
- Using a Ag/In ratio of 1/5, the PL spectrum shows an emission band centered at 601 nm as well as a lower energy emission related to defects.
- The defect-related emission disappears after the ZnS shell capping and a blue-shift of the PL emission at 563 nm is observed due to the alloying with Zn^{2+} ions. The quantum yield of these nanocrystals reaches 67%.

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2018

Powder rheology : measurement systems, modeling and formulation

Assia SAKER (3rd year)

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Axe Product Engineering | EMMAD

Keywords: Powder technology, Powder flow, Storage, Flowability, Formulation, Powder rheometer, Particle size distribution, , Energy of vibration, packing behavior.

General context, scientific issues

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

Objectives and stakes

- ✓ Understand the interactions between particles and between particles and equipment.
- ✓ Achieve a multi-scale characterization of flowability and rheological behavior of powders.
- ✓ Explain, the change in flowability classification according to the different techniques.
- ✓ Access to packing properties by various techniques available in the laboratory.
- ✓ Study the impact of flow regulator on powder flowability

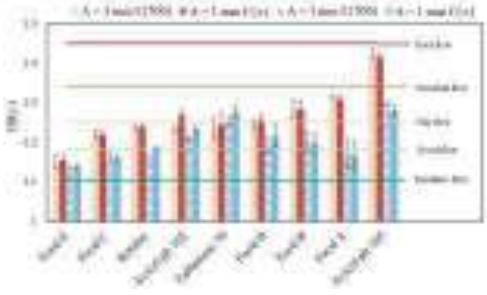
Methodology / Experimental approach

To study the effects of shapes and sizes, a wide range of pharmaceutical, cosmetic and food powders was selected. Powder characterization is carried out from the analysis of the particle size distribution using laser granulometer Mastersizer 2000 and of the powders morphology by imaging with a scanning electron microscope.
The characterization and classification of flowability of powders are usually based on angle measurements or packing properties. One aim of the project is to obtain powder flow properties by using powder rheometers.

Illustration: MEB Micrograph Retalac particles

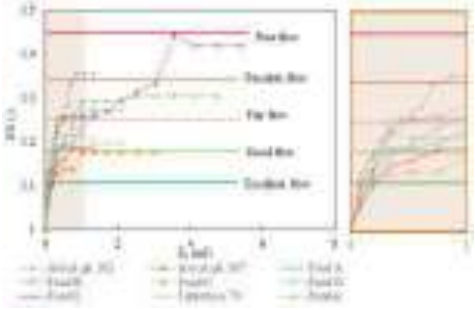
Main results

Hausner ratio (HR) used as index of flowability shows in previous works an interdependence between the initial state of powders and their physicochemical characteristics, however, in our work this index is closely related to dynamic parameters (amplitude, frequency).



A: amplitude (mm), C: compactness (-), and N: number of taps.

One of our techniques, allowing the control of mechanical vibrations, clearly shows that, depending of the energy of vibration E_v, the classification of powder can change.



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2018

Metal-Organic Framework templated synthesis of doped-TiO_2 or TiO_2-based heterostructures for visible-light promoted photocatalysis

Batukhan TATYKAYEV (Researcher)

Raphaël SCHNEIDER
Axe Product Engineering | EMMAD

Keywords: MIL-125(Ti), Fe^{3+} doping, calcination, heterostructured photocatalysts

General context, scientific issues

Increasing contamination and deterioration of water quality has been a serious concern for human health and sustainable development [1]. Therefore, the development of new highly efficient photocatalysts for water treatment are very relevant today.

Objectives and stakes

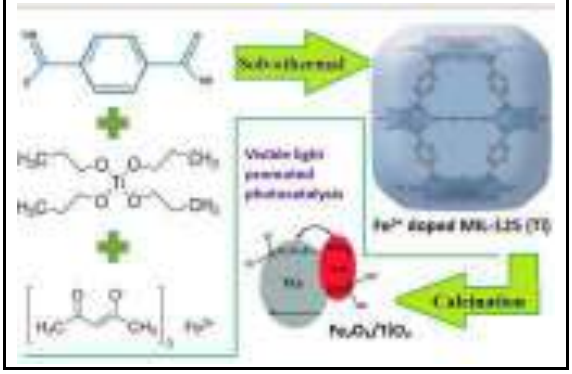
Hierarchical anatase TiO_2 can be synthesized from titanium-based metal-organic framework (MOF) precursor followed by calcination in air [2]. The synthesis of bimetallic MOFs containing both Ti(+4) and metallic cations like Fe^{3+}, Mn^{2+},... and their thermal decomposition have never been studied.
We plan to develop efficient, scalable and economic approaches to synthesize doped TiO_2 particles or heterostructures like TiO_2/Fe_3O_4 that not only absorb visible light (> 400 nm) but that also have suitable band positions to drive photocatalytic reactions.

Methodology / Experimental approach

Fe(+3)-doped MIL-125 particles were prepared by a solvothermal method according to a modified synthetic protocol reported by Yu et al. [3]. The synthesis was conducted by reacting terephthalic acid dispersed in DMF with titanium (IV) propoxide (TPOT) and iron (III) acetylacetonate (Fe(acac)3) in a teflon-lined stainless-steel autoclave for 48 h at 423 K under autogenous pressure.

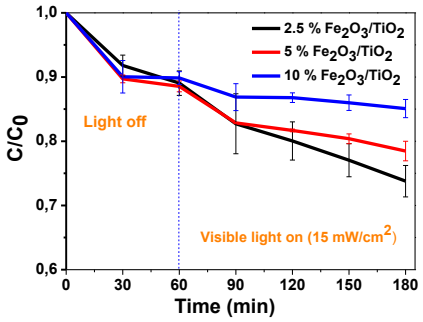
10, 5, 2.5 and 1% Fe-doped MIL-125(Ti) materials were prepared by varying the molar ratio between TPOT and Fe(acac)3.
Fe-doped MIL-125(Ti) particles were transformed into hierarchical Fe2O3/TiO2 nanocomposites by a thermal treatment at 450°C for 2 h to remove organic compounds.
All materials were characterized by SEM, TEM, XRD, UV-visible absorption,...

Illustration: *MOF templated synthesis of Fe_2O_3/TiO_2*



Main results

Fe_2O_3/TiO_2 nanocomposites were tested as photocatalyst for the degradation of the Orange II dye under visible light irradiation.
The influence of the calcination conditions of the Fe(+3) doped MIL-125 and of the doping percentage in Fe on the photocatalytic activity of Fe_2O_3/TiO_2 materials was investigated. The highest photocatalytic activity was observed for materials calcinated at 450°C and for 2 hour and using 2.5% doping in Fe.



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2018

Synthesis processes, properties and applications of bio-based engineering elastomers

Xinxin ZHOU (3rd year)

Guo-Hua HU, Liqun ZHANG
Axe Product Engineering | GP2

Keywords: Synthesis, properties, engineering applications, bio-based elastomers, green tires, green chemistry, nanocomposites, sustainable development

General context, scientific issues

Globally, we are facing a massive growth in the number of urban vehicles. This growth comes at the cost of enormous fuel consumption, CO_2 emissions and air pollution. Tires are an essential component of all urban and rural vehicles. Synthetic elastomers used in tires now are mainly derived from petrochemicals, which are not sustainable. The global climate change (global warming) and air pollution (smog or haze) strike directly at the intersection of societal environmental demands and economic needs. Environmentally-friendly solutions must be found. To meet this target, renewable elastomers must be developed and non-renewable carbon black must be replaced with non-petroleum-based fillers, like nano-silica.

Objectives and stakes

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

• Itaconates were prepared by esterification of itaconic acid using the mono-alcohols.

• Bio-based elastomers were synthesized through redox emulsion polymerization of itaconates and dienes.

• Novel green tires were fabricated by combining molecular design of bio-based elastomer and *in-situ* modification technology of silica.

Methodology / Experimental approach

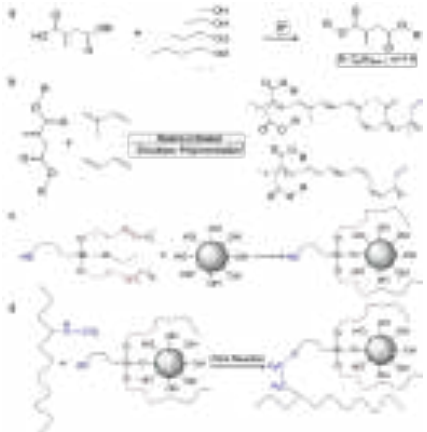

Illustration: The integrated bio-based chemicals-synthesis-low roll-resistance green tire pathway for resource sustainability and environment protection.

Main results

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

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

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