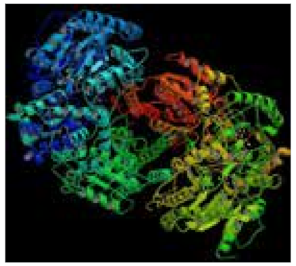
MECHANICAL ENGINEERING | PHYSICS | PRESERVATION OF THE ARCHITECTURAL HERITAGE | SPATIAL PLANNING AND URBAN DEVELOPMENT | STRUCTURAL SEISMIC AND GEOTECHNICAL ENGINEERING | TECHNOLOGY AND DESIGN FOR ENVIRONMENT AND BUILDING | TERRITORIAL DESIGN AND GOVERNMENT | AEROSPACE ENGINEERING | ARCHITECTURAL AND URBAN DESIGN | ARCHITECTURAL COMPOSITION | ARCHITECTURE, URBAN DESIGN, CONSERVATION OF HOUSING AND LANDSCAPE | BIOENGINEERING | BUILDING ENGINEERING | DESIGN | DESIGN AND TECHNOLOGIES FOR CULTURAL HERITAGE | ELECTRICAL ENGINEERING | ENERGY AND NUCLEAR SCIENCE AND TECHNOLOGY | ENVIRONMENTAL AND INFRASTRUCTURES ENGINEERING | **INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING** | INFORMATION TECHNOLOGY | INTERIOR ARCHITECTURE AND EXHIBITION DESIGN | MANAGEMENT, ECONOMICS AND INDUSTRIAL ENGINEERING | MATERIALS ENGINEERING | MATHEMATICAL MODELS AND METHODS IN ENGINEERING

# PhD Yearbook | 2016

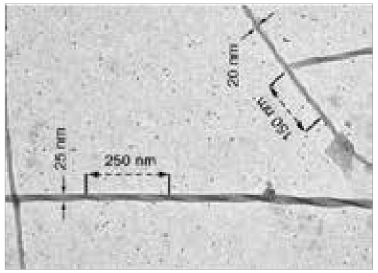
# DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

Coordinator:
**Prof. Alessio Frassoldati**

The Doctoral Program in Industrial Chemistry and Chemical Engineering (***CII***) is designed for students aiming to get a deep expertise on chemical processes and on material processing either as the inherent *research* or in the *process design and development* activities. The program is the ideal extension of the *Laurea Magistrale* degrees in *Chemical Engineering*, *Safety and Prevention Engineering*, *Materials Science*, *Material Engineering*, *Industrial Chemistry* and *Chemistry*, but it is also open to graduated in other scientific disciplines.



Structure simulation of Nitrogenase enzyme for N2 conversion to NH3

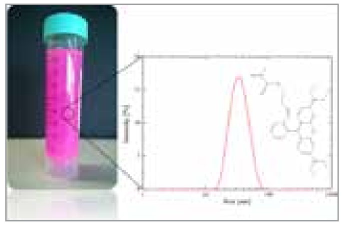


Amyloidal peptide nanohelices in solution as ordered nanomaterials (Nature Commun. 2015, 6:7574, DOI: 10.1038/ncomms8574)

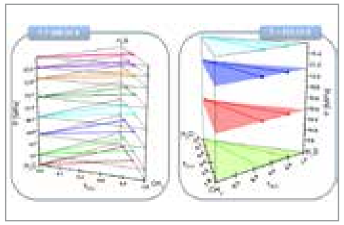
The general topic for the doctoral program in Industrial Chemistry and Chemical Engineering is the application of the chemical and physical knowledge to all the activities related to the synthesis, design, production and transformation of chemical substances and materials (like advanced inorganic, polymers and biomaterials). These studies involve not only the synthesis processes but also the related plants, here analyzed starting from the laboratory tests and the pilot plant experiments up to the industrial size ones, always including the careful evaluation of the related energetic, safety and environmental issues.

The final goal is to provide to the PhD student the tools and the skills: (1) to design and manage industrial processes at any size scales; (2) to develop new technical applications and (3) to create and to characterize new products and services.

The ***CII*** program covers three years for an overall amounts of 180 credits. The responsibility of the organization and of the contents of the doctoral program is attributed to the Professors Committee (PC). At the beginning of the Doctoral program, a tutor and a thesis advisor is assigned to each student. The tutor has a supervisor function during the whole doctoral program, whereas the thesis advisor is responsible for the thesis work.



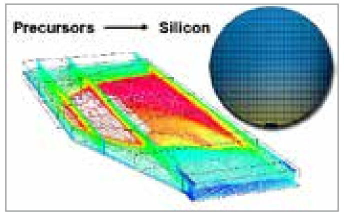
“Biocompatible polymer nanoparticles functionalized with a fluorescent dye for in vivo imaging studies”



VLE and VLLE measurements for the system CH4-H2S-H2O.

The PC defines a specific curriculum for each student, on the basis of the tutor suggestions. The curriculum has to be designed in order to both cover deficiencies in the student scientific formation and to give a high-quality technical and scientific preparation.

Since 2001 (XVII cycle) the ***CII*** program graduated more than 100 students, being ~80% now working in industry and the remaining in the university or government research centers. These data demonstrate the great link existing between the performed researches and the industry. In fact, numerous the research topics were directly supported by industrial companies, like ENEL, LPE Epitaxial Technology, Bracco, Flamma, Mapei, Solvay Specialty Polymers, RSE, Isagro, Tecnimont, Biochemtex, Pirelli.



Simulation of a chemical vapor deposition reaction for silicon films deposition

Hazardous gas dispersion simulation from an industrial accident

## THE REFERENCE COMMITTEE

| | |
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| Giancarlo Terraneo | Enrico Tronconi | |

## GRANTS

Solvay Specialty Polymers Italy SpA, IIT, Pirelli, MTU Friedrichshafen (Motoren Turbinen Union)

# MULTI-ZONE MODEL FOR HCCI COMBUSTION

**Mattia Bissoli** - Supervisor: prof. Tiziano Faravelli

Today, car manufacturers are facing many different problems in terms of engine technology.

The choice of the energy source as fuel is no longer only a matter of performances, but many other factors play a fundamental role, such as fuel availability, price, geopolitical aspects and the renewed consciousness of the public opinion about the environmental impact of these choices. Fossil fuels are actually still the primary energy resource and their use in the transportation sector represents one of the largest source of pollutant emissions. In recent years, many different solutions have been proposed with the aim of guiding the transportation sector towards a cleaner future, such as electric vehicles, hydrogen propulsion, etc.

However, many of these solutions are facing technical barriers and economic constraints, highlighting that Internal Combustion (IC) engines will have a primary role in the transportation sector for many years. The targets of higher efficiency and simultaneous reduction of pollutant emissions can be achieved by means of new Low Temperature (LT) combustion techniques, like the Homogeneous Charge Compression Ignition (HCCI), where a homogeneous mixture of air and fuel is auto-ignited due to compression.

Nevertheless, the nearly constant-volume combustion at the base of this technology, due to the very rapid Rates of Heat Release (HRR), causes high rates of pressure rise (PRR). This aspect is critical for the HCCI combustion, because PRR increases with increased fueling, defining the maximum high-load limit achievable by the engine. When high fueling rates are required, PRR can become so rapid that it results in unstable combustion forms and knock.

Today, this is one of the most significant technical barriers limiting the adoption of HCCI technology.

The present PhD thesis developed a new comprehensive model able to describe multiple aspects of the HCCI combustion by taking into account all the relevant physical phenomena and engine-related elements involved in the process. A fundamental aspect is the capability to investigate the chemical kinetics ruling the characteristic combustion behaviors of HCCI, as well as the capability to predict pollutant emissions and highlight their formation pathways.

The model is based on a multi-zone quasi-dimensional approach, where the reacting volume is divided into a user-defined number of sub-domains called “zones”. This configuration has been chosen for the possibility to describe the thermal stratification with a reduced computational effort. Each zone can interact with the neighboring ones through mass and heat fluxes, both laminar and turbulent.

The model also describes the effect of Residual Burned Gases (RBG), Exhaust Gas Recirculation (EGR) and crevices, whose role on combustion phasing, species profiles and pollutant emissions is highlighted by the comparison of model predictions with the experiments obtained from the Drexel engine.

The focus is on combustion, thus only the compression and expansion strokes of a four-stroke cycle are described during a simulation cycle. The auto-ignition mechanism ruling the ignition in HCCI engines gives to chemical kinetics a very important role. For this reason, the model is specifically designed to manage detailed kinetic mechanisms, which are mandatory for the correct prediction of the auto-ignition phenomena and the in-cylinder speciation.

Furthermore, analysis tools like the Rate of Production and the Sensitivity Analysis have been implemented in the model in order to show the interactions between system conditions and chemistry, leading to pollutant formations and emissions, as well as to identify the reaction pathways. The Sensitivity Analysis in this multi-zone model is made difficult by the differential-algebraic nature of the system. For this reason, a proper mathematical formulation has been developed.

Experiments showed that a certain level of thermal stratification is always present in HCCI engines, and it helps regulating the PRR.

Thus, its description is mandatory for having reliable results. A wall function model has been successfully adopted for the first time in a multi-zone model for the description of the heat exchanged between the system and the boundaries, resulting in a significant improvement of the model descriptive capabilities in the near-wall region compared with global approaches. Its reliability has been demonstrated comparing model predictions with experimental data and CFD results obtained from four different engines under several different operating conditions and with different geometries. The coupling of this new heat transfer model with a simplified turbulence model allows the present multi-zone model to correctly reproduce the thermal stratification occurring in HCCI engines.

PRR can be also mitigated by delaying the combustion phasing. Although this solution can result in combustion instabilities, its coupling with boost pressure, EGR and a lower intake temperature makes this technique an effective solution for fuels with a strong LT reactivity, thanks to the so-called Intermediate Temperature Heat Release (ITHR) phenomena. ITHR consists in a slow heat release associated with early pre-ignition reactions occurring at temperatures between the typical low-temperature and the hot ignition, sufficient to prevent the system temperature to drop during expansion.

The analyses on the Sandia and UC Berkeley engines highlighted the capability of the model to reproduce the thermal stratification and the experimental PRR, as well as to correctly describe the ITHR phenomena in terms of pressure, combustion phasing and duration for several different boost conditions. Sensitivity and Rate of Production analyses confirmed the importance of $CH_3$, $CH_3O_2$ and $HO_2$ in the ITHR. Furthermore, they highlighted the role of n-heptane as pilot fuel in biogas mixtures, confirming that even if the oxidation of $CH_4$ is the main source of the heat release observed, n-heptane promotes the LT oxidation of methane by increasing the production of $H_2O_2$.

Lastly, the model emphasized the role of $H_2O_2$ concentration as a reliable ITHR index when n-heptane is used.

Emissions from HCCI combustion of different biofuels suitable as gasoline and diesel surrogates has been investigated comparing model predictions with data from the Cooperative Fuel Research (CFR) engine of Michigan University. The multi-zone model correctly reproduced the two-stage ignition behavior of all the fuels tested (n-butanol, methyl-decanoate, methyl heptanoate and methyl hexanoate) in terms of phasing and emissions of the main species, highlighting the presence of a Critical Compression Ratio (CCR) above which emissions of partial combustion products are negligible. Moreover, the model confirmed that this CCR is fuel dependent, and mainly related with the extent of its LT reactivity.

Sensitivity and Rate of Production analyses clarified the pathways leading to pollutant formation and emissions, confirming the findings of previous works. In particular, the role of decarboxylation reaction in the $CO_2$ production during LT reactivity, the different reactivity of the saturated methyl esters in this combustion region as a function of the alkyl chain length, as well as the reasons of the reduced LT reactivity of n-butanol compared with traditional fossil fuels, and the role of n-heptane in promoting the reactivity of the mixture.

Numerical aspects play a fundamental role as well: suitable solvers and advanced programming techniques are used in order to manage the high stiffness and to reduce the computational effort.

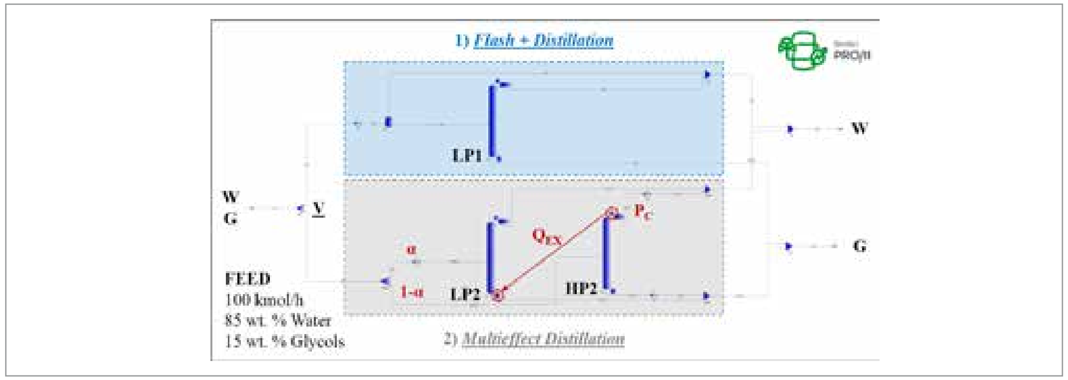
All the improvements introduced by the present work constitute a step forward to getting reliable predictions of auto-ignition and emissions from HCCI engines.

Due to its flexibility, it is expected that this model could be easily adopted to model other engine-like systems, such as Rapid Compression Machines (RCMs).

# GREEN ETHYLENE GLYCOL: MINLP DOWNSTREAM PROCESS OPTIMIZATION AND MULTI-SCALE SIMULATION OF GASIFICATION PROCESSES

**Michele Corbetta** - Advisor: Prof. Sauro Pierucci

This Thesis deals with the modeling, simulation and optimization of the GREG™ (GReen Ethylene Glycol) process for the production of 2nd generation bio-based glycols, currently in development at Biochemtex S.p.A. Two main topics have been addressed: the GREG™ downstream MINLP (Mixed-Integer Non-Linear Programming) process optimization, and the kinetic modeling of gasification processes for the supply of hydrogen to the GREG™ catalytic section.
The GREG™ technology allows to produce ethylene (EG) and propylene (1,2-PG) glycols from purified C5 sugars with a two-step catalytic conversion process (hydrogenation/hydrogenolysis). At the outlet of the catalytic section, unreacted $H_2$ is separated and recycled, while the liquid stream is purified in a downstream section to produce high purity glycols. The purification is achieved in three steps: dewatering, separation of the heavy cut, and final glycols purification. The dewatering occurs reducing the pressure in a flash drum followed by a distillation column. Separation of the heavy cut is accomplished by using an Agitated Thin-Film Evaporator, where glycols are evaporated and removed from the heavy species. Finally, a distillation train allows to purify raw glycols from butanediols (BDOs).
The high heat of vaporization of water determines high downstream OPEX. For this reason, attempts to optimize and thermally integrate the purification step result in a relevant lowering of the production costs that reduces the economic gap with equivalent fossil-based products.
During a visiting period at Carnegie Mellon University (USA), a new MINLP algorithm has been developed, coupling the process modeling environment of the commercial simulator PRO/II® (Schneider Electric) with the optimization environment of GAMS®. Both continuous and integer decision variables are optimized under the Generalized Disjunctive Programming framework. The algorithm requires a superstructure, the propositional logic to define its topology, a PRO/II® flowsheet, a set of bounded decision variables, nonlinear constraints, and an economic objective function. The optimization problem is solved with a decomposition strategy based on the Logic-Based Outer Approximation algorithm that involves NLP subproblems solved with the BzzMath Derivative Free Optimizer, and MILP master problems solved in GAMS®.
The model-based optimization is strengthen by the experimental feedback of the Biochemtex laboratory for the definition of new reliable VLE thermodynamic models for the nonideal liquid mixtures through a nonlinear regression, and by the comparisons with distillation and evaporation experimental data from the Biochemtex pilot plant.
The dewatering step is optimized considering two different technologies (Figure 1). Namely, atmospheric distillation and multieffect distillation with two heat integrated columns operated at different pressures. The optimization targets are to select the best technology and to optimize the selected columns. Three constraints allow to specify glycols recovery, water purity and temperature feasibility for the heat transfer. It turns out that the multieffect distillation is the best technology. The heat integration in the optimized configuration is greater than the 99 % of the condenser duty, with a steam utility cost saving of 122,289 $/y, while total annualized costs of LP2 and HP2 columns are 169,813 and 163,997 $/y respectively.
The heavy cut removal step is analyzed with the development of a rate-based model that was validated with experimental data from the Biochemtex evaporator pilot plant and included as a custom unit in PRO/II®. A sensitivity analysis allows to assess the role of the main design and operating parameters on product recoveries.
Finally, the rigorous design of the distillation sequencing for the glycols purification step is addressed. The design is achieved by considering a superstructure for the quaternary mixture (composed by glycols and BDOs) with 10 atmospheric columns, and optimizing both the selection of the columns and their conditional trays, as well as two specifications. Four implicit inequality constraints are introduced to satisfy minimum purities and recoveries. The selected configuration is the sequence of columns that first realize the central cut between 1,2-PG and EG and then purify glycols from BDOs.
The H2 supply for the catalytic section is assessed developing simulation tools and kinetic models of biomass/coal gasification processes. Multi-step kinetic models are embedded in a particle model, along with gas-solid and secondary gas-phase reactions in order to simulate gasifiers at the reactor scale and to assess their performance in syngas production.
The chemical evolution of the system requires a kinetic description at three levels: solid fuel pyrolysis, residual solid gasification and combustion, and secondary gas-phase reactions. The kinetic model of biomass pyrolysis, updated in this Thesis, involves the superposition of sub-mechanisms for each pseudocomponent: cellulose, hemicellulose and lignins. Products of the fragmentation reactions include several species belonging to permanent gases, oxygenates and char. Depending on temperature and residence time, secondary reactions are responsible for the successive pyrolysis and oxidation of volatiles. The POLIMI kinetic scheme is used for this purpose (about 450 species and about 15,000 reactions).
The simulation of a gasifier requires also the description of transport processes at the reactor scale.
The dynamic model of the gasifier implements a Finite Volume Method (FVM) with a Representative Particle Model (RPM) with two levels of spatial discretization.
The first one is the particle radial discretization, while the second is the reactor axial discretization. The updraft gasifier is modeled through a cascade of elementary reactor layers, where the solid fuel is fed from the top and it encounters the rising gas stream fed from the bottom. During the residence time, particles are progressively dried, pyrolyzed and gasified, leading to the residual char and to a gas stream rich in H2. The resulting stiff DAE system overcomes several thousands of equations and it is solved with the BzzMath library.
Results of the updated multi-step kinetic model of biomass pyrolysis are compared to experimental results of 3 independent sets of centimeter-scale experiments. Temperatures, mass losses, and rate of production of several gaseous and light tars are included in the comparisons.
Predictions and experiments agree qualitatively, and in most cases have reasonable quantitative agreement. The detailed models have been subsequently adopted for the modeling of updraft gasifiers. Simulations are analyzed and compared with 2 sets of experiments referring to the lab scale gasifier in Grieco & Baldi (2011) and to the Sotacarbo S.p.A. pilot plant with a reasonable agreement.



1. Superstructure for the optimization of the dewatering task of the GREG™ downstream process.

# DOWNHOLE ACID GAS REMOVAL FROM NATURAL GAS

**Giorgia De Guido** - Advisor: Prof. Laura Annamaria Pellegrini
Tutor: Prof. Isabella Nova

Natural gas has been recently playing an important role in the energy mix and it is poised to enter a "golden age", being the fastest growing of all fossil fuels. Although natural gas is mostly considered to be a clean fuel with respect to the emission of pollutants from its combustion, the raw natural gas found in reservoirs is not necessarily free of contaminants. Indeed, natural gas consisting primarily of methane contains some other compounds, such as hydrogen sulfide and carbon dioxide, which are responsible for its sour or acidic nature. The presence of these impurities requires their removal in order to meet pipeline quality standard specifications, to avoid equipment corrosion and to enhance the calorific value of natural gas.

Typically, acid gas treating is performed in facilities built at surface locations by means of a purification technology that can be chosen among the numerous ones developed for this purpose. An alternative to this would be to develop subsurface technologies which allow to possibly separate the acid gas undesired compound(s) directly downhole. Some solutions have been presented in the literature for acid gas removal from a natural gas stream to be performed in the well hole, which are mainly based on the use of membranes.

This thesis aims at evaluating the feasibility of a new idea consisting of performing natural gas purification by means of physical absorption into the gas production casing using water as the absorbing agent. The high pressures encountered downhole make the use of water as liquid absorbent worth considering and the acidic species can possibly be left underground, thus anticipating their removal with respect to surface processing.

To evaluate the possibility of a real application for this idea, on one side it has been necessary to study the fluid dynamics which establishes in the gas production casing when water is contacted with the ascending raw natural gas to be sweetened. Since the facility in which the absorption process would take place can be conceived as a bubble column in which a gas phase (*i.e.*, the raw natural gas) is contacted with the liquid phase, in cooperation with the Energy Department of Politecnico di Milano flow phenomena have been investigated in a bubble column having the same geometric features of the real gas production casing. Due to its diameter (*i.e.*, 0.24 m), it belongs to the class of large diameter vertical pipes for which there exist very few works in the literature dealing with flow patterns in counter-current operation. At this first stage of the project, the column has been operated at atmospheric pressure and the attention has been devoted to measurements of the overall gas holdup, which is a key parameter in the characterization of transport phenomena in bubble columns. In all the experiments, air has been used as the dispersed phase and several liquids (*i.e.*, water and aqueous solutions containing different concentrations of sodium chloride, ethanol and monoethylene glycol) have been employed as the continuous phase in order to investigate the effect of liquid properties on the gas holdup. In all the experimental runs the liquid phase has been supplied in batch form and with water some runs have been also conducted with the liquid phase moving counter-currently to the gas phase. Two types of correlation have been studied to reproduce the gas holdup experimental data. The final correlation proposed in this work and used to evaluate the volumetric mass transfer coefficient allows to reproduce the peak in the gas holdup versus the composition that has been observed for the system air-aqueous solutions of monoethylene glycol and it also accounts for the effect of the liquid superficial velocity.

Furthermore, in order to achieve a better knowledge of the thermodynamic multiphase behavior of acid gas mixtures with water, the ternary system $CH_4$-$H_2S$-$H_2O$ has been experimentally studied at the CTP - MINES ParisTech. It has been chosen as representative of sour natural gas mixtures since surprisingly, despite its importance, very few multiphase equilibrium data can be found in the literature for it. In particular, no vapor-liquid-liquid equilibrium (VLLE) data are available. Therefore, in addition to two-phase vapor-liquid equilibrium conditions, three-phase VLLE conditions have been determined, by setting up a proper experimental procedure. These data have allowed to identify the region where the second $H_2S$-rich liquid phase can form (Fig. 1) in addition to the vapor and $H_2O$-rich liquid phase for the considered temperature levels: such region is shrunk as pressure increases, for a given temperature, and it gets smaller for increasing temperatures. Moreover, since both $CH_4$ and $H_2S$ are known to be hydrate formers, hydrate dissociation point data have been determined as well, by means of the well known isochoric method. The experimental work has allowed to state at which temperature and pressure conditions the investigated downhole natural gas purification process should be operated to avoid hydrate formation as well as the existence of a second $H_2S$-rich liquid phase. The two binary systems $CH_4$-$H_2O$ and $H_2S$-$H_2O$ and the ternary system $CH_4$-$H_2S$-$H_2O$ have been also studied from a modeling point of view by Gibbs free energy analysis. An analytical Equation of State proposed in the literature for describing the phase behavior of the three thermodynamic states (solid, liquid and vapor) of matter has been chosen for the representation of these three phases and it has been combined with the classical statistical thermodynamic approach to hydrate phase equilibria to also account for the hydrate phase. Some modifications to the relations proposed in the literature to express the difference in the chemical potential of the empty hydrate lattice and that of pure water have been applied to improve predictions of hydrate formation conditions for simple hydrates of methane, as well as of hydrogen sulfide. The thermodynamic approach has been also used to predict the fluid-equilibrium conditions determined experimentally, as well as the hydrate dissociation points, obtaining good results and better predictions of the hydrate formation pressure than those given by other thermodynamic models considered for comparison.

The results of the fluid dynamic and of the thermodynamic study have been applied to carry out a preliminary evaluation of the performances of the absorption process for the removal of $H_2S$ from acid natural gas by means of water scrubbing. It has been found that it is possible to reduce the $H_2S$ content from 5-15 mol% to the commonly accepted value to meet pipeline specifications, considering flow rates compatible with reinjection into the reservoir for water.

A study of the fluid dynamics under pressure and additional multiphase equilibrium data for the ternary system $CH_4$-$H_2S$-$H_2O$ would allow to better assess the feasibility of the investigated downhole process for the removal of acid gases from natural gas.

1. Measurements of three-phase vapor-liquid-liquid equilibrium conditions for the system $CH_4$-$H_2S$-$H_2O$.

# SIRNA DELIVERY THROUGH POSITIVELY CHARGED POLYMER NANOPARTICLES

**Luca Dragoni** - Supervisor: Prof. Davide Moscatelli

The aim of this PhD thesis is the synthesis, characterization and biological validation of positively charged polymer nanoparticles (NPs) suitable for the delivery of siRNA in biomedical applications. The NPs have been designed to satisfy the following important requirements for use in the delivery of polynucleotides (e.g., siRNA):

- The possibility of synthesizing stable and monodispersed NP latexes with final dimensions in a range of values suitable for intravenous delivery (20-250 nm).
- The development of a reliable and reproducible process for NP synthesis.
- The possibility to produce positively charged NPs without the use of surfactants. Because the final target is the delivery of negatively charged siRNAs, the presence of positive charges on the NP surface are indispensable for the formation of siRNA-NP complexes.
- The production of biodegradable NPs. To be used for biomedical applications, the NPs have to be biodegradable so they do not accumulate in the body. Furthermore, biodegradability is a key parameter for the possibility of tuning and shortening the release time of the siRNA.
- The possibility of producing PEGylated NPs. A great challenge in the use of NPs for intravenous drug delivery is the mitigation of the opsonization process in the bloodstream carried out by the mononuclear phagocyte system. It is known that NP characteristics affect opsonization itself; specifically, it is well known that positively charged NPs are much more sensitive to opsonization than neutrally charged NPs. A common way to protect the NPs from uptake by macrophages is the functionalization of the NP surface with hydrophilic moieties.

To meet all these criteria, NPs have been produced via free radical emulsion polymerization (FREP), a chemical process both investigated in the literature and widely used in industry. This synthetic route was selected because it may facilitate control of some key features of the final NPs such as their size, surface charge, dispersity, etc.

At first, NP synthesis was carried out by a two-step process. The first step was the synthesis of biodegradable ester-based macromonomers obtained through the ring opening polymerization (ROP) of the cyclic esters of lactide (LA) and ε-caprolactone (CL), which was performed following well established procedures from the literature. The presence of a vinyl group makes this macromonomer suitable for polymerization via FREP to obtain biodegradable NPs. The co-polymerization of the CL-based macromonomers with [2-(methacryloyloxy)ethyl] trimethyl-ammonium chloride (HEMA-Ch) allowed surfactant-free positively charged NPs to be obtained, which could bind to the negatively charged siRNA.

HEMA-Ch can be considered as a surfmer, which is a molecule that is able to stabilize the NPs similar to a surfactant and can be simultaneously covalently incorporated into the polymer chains during polymerization due to the presence of a reactive double bond. The final product of the FREP consists of a poly(HEMA) backbone with biodegradable polyester side chains grafted to it; in PEGylated NPs, polyethylene glycol methyl ether methacrylate (PEGMA$_m$) chains are present.

NP degradation begins with the hydrolysis of the ester bonds that link the CL units that constitute the grafted chains. As they progressively lose the CL units, the NPs become more hydrophilic, favoring the swelling process until the degradation products as well as the remaining water-soluble polyHEMA are obtained.

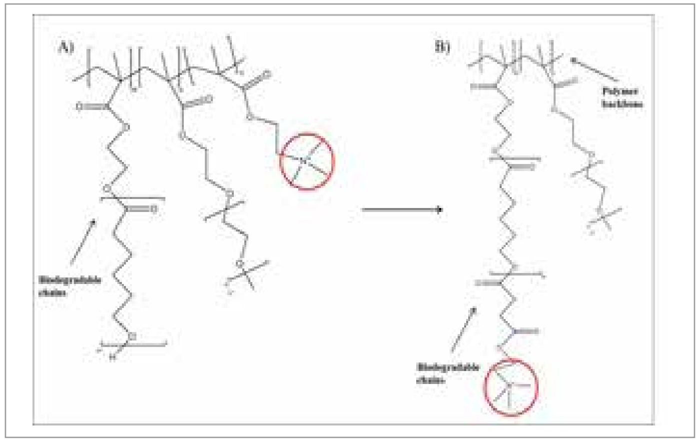
Once the NPs have been synthesized and their biological compatibility validated, some experiments using a therapeutic siRNA were carried out to test the efficiency of the NPs as effective carriers for siRNA. Obtaining significant silencing of a target gene is a great challenge because the carriers must be designed to perform different simultaneous functions, as follows:

- Protect the siRNA from degradation that easily occurs in biological environment (e.g., in the cell cytoplasm).
- Make the cellular internalization of siRNA possible.
- Release biologically active siRNA from the NP surface after cellular internalization.

Accordingly, we wondered why we had not achieved the silencing of the target gene despite the fact that NPs could carry and release undamaged siRNA inside the cell. We concluded that the problem was the final NP structure. In fact, in the NPs we produced, the siRNA is directly connected to the NP polymer backbone, which is the last part of the NPs that degrades. This could allow the formation of complexes between siRNA and poly-HEMA that constitute the polymer backbone, making the siRNA unable to perform its biological function.

To solve this problem, we started to functionalize our CL-based macromonomers using choline chloride to use these new positively charged macromonomers as surfmers for NP synthesis instead of HEMA-Ch. For this use, the positive charge would be located at the end of the biodegradable polyester side chain rather than directly connected to the polyHEMA backbone (**Figure 1**). Accordingly, as soon as the degradation mechanism begins with the hydrolysis of the ester bonds that link the CL units constituting the biodegradable side chains, the siRNA that is electrostatically bound to the positive charges will be immediately released from the NP surface and thus will be free to perform its biological function.

The positively charged functionalized macromonomers were obtained through a three step process that involved the acylation of the HEMA-CL$_n$ macromonomers followed by a Steglich esterification. Obtained macromonomers could be employed as surfmers instead of HEMA-Ch for the synthesis of positively charged NPs.



1. Difference between the structure of HEMA-Ch+-based NPs (A) and NPs synthesized using the novel Ch+-based positively charged macromonomers (B).

The NPs were synthesized via FREP under both batch emulsion polymerization (BEP) and monomer-starved semi-batch emulsion polymerization (MSSEP) conditions. To improve the stability of the NP suspension, especially after siRNA adsorption on the NP surface, PEGMA$_m$ was used as a steric co-surfmer. The final FREP product consisted of a poly(HEMA) backbone with both PEGMA$_m$ chains and biodegradable polyester side chains grafted to it; in this product, the positive charge was located directly at the end of the biodegradable side chains.

Subsequent, tests were carried out using a therapeutic siRNA to assess the efficiency of the NPs as an siRNA carrier.

These novel NPs were used to obtain significant silencing of a specific target gene, confirming the effectiveness of the NPs produced via positively charged macromonomers, such as siRNA carriers. In collaboration with the M. Negri Institute for Pharmacological Research, tests to optimize some parameters, such as the NPs/siRNA ratio, are still ongoing, but the results achieved so far demonstrate that the NPs are promising carriers for the effective delivery of siRNA or other polynucleotides in biomedical applications.

# THE ACTIVITY OF CU-CHA IN COMPARISON TO MORE CONVENTIONAL SCR CATALYSTS

## Amirreza Fahami

In accordance with the tendency toward decreasing of Carbon Dioxide ($CO_2$) emissions due to the well-known Green House Gases (GHG), and other environmental emissions problems, lean burn engines, e.g. diesel engines, have shown a promising future for Internal Combustion (IC) engines. However, the emission regulation of diesel engines is continuously becoming more and more stringent. As a consequence, a typical Exhaust Aftertreatment System (EATS) of a diesel engine consists of different components. The first part of the exhaust treatment of a diesel engine takes place in a converter, referred to as Diesel Oxidation Catalyst (DOC). The main aim of this step is oxidizing carbon monoxide (CO) and unburned hydrocarbons (HC) in the exhaust stream. Another important task of DOC is oxidizing NO to $NO_2$ which is more preferable in the converters downstream of DOC. Right after DOC, a Diesel Particulate Filter (DPF) is placed in order to abate particulate matter and soot in the exhaust stream. The trapped soot can be consequently oxidized by $NO_2$ which was produced in the previous section, DOC. Another converter, either a lean NOx trap (LNT) or a selective catalytic reduction (SCR) component reduces NOx to nitrogen. In the case of employing ammonia as the reducing agent, the SCR procedure ends up with an ammonia slip catalyst to remove any excess of ammonia. The described system guarantees a very efficient DeNOx activity which fulfills EURO-6 limitations at temperatures higher than ca. 180°C, the minimum temperature for the system in order to start the urea injection.
Selective Catalytic Reduction (SCR) of nitrogen oxides, NOx (x = 1, 2) has been determined as an efficient technique to convert toxic NOx emissions from diesel engines to nitrogen and water. The main part of NOx emissions from a diesel engine is nitric oxide (NO) and consequently the so-called Standard SCR reaction (R.1) with equimolar consumption of NO and $NH_3$ contributes significantly to the DeNOx treatment:

$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O$ **(R.1)**

When nitrogen dioxide ($NO_2$) is present in the gas mixture, it has been shown that the catalytic reduction occurs via a different reaction, Fast SCR (R.2), where the reduction of NOx by ammonia takes place at a relatively lower temperature and higher reaction rate. The placement of DOC in the upstream of the SCR converter improves the share of Fast-SCR compared to Standard-SCR.

$2NH_3+NO+NO_2 \rightarrow 2N_2+3H_2O$ **(R.2)**

On the other hand, due to the proximity of DPF to the SCR unit, in the time of DPF regeneration, the SCR catalyst will be exposed to a gas flow with very high temperature (> 650°C). Typical SCR catalysts suffer from this severe condition and become inactive after short time due to the harsh ageing, and consequently show a limited operating life time.
The state-of-the-art in SCR catalysis is related to molecular sieves with the chabazite structure (CHA), like SSZ-13, which are ion-exchanged with copper. This class of SCR catalysts have shown a desirable resistance to harsh ageing and that is why they have received the attention of many researchers. Due to its reliability, Cu-SSZ-13 has been utilized vastly in the aftertreatment industry. Despite commercial applications of Cu-SSZ-13, the nature of the active sites, the interaction of the reactants in different reaction regimes, and the mechanism of the SCR reactions have not yet been fully understood. There is an agreement on the Redox cycle of copper in Standard SCR. So far, however, several mechanisms for the SCR reactions have been proposed by many research groups. The basis of this controversial point of view is the nature of copper and the difficulties of monitoring the active sites under reaction conditions. Many studies have been carried out to observe the character of the active phase of copper, suggesting copper dimers (e.g., $[Cu\text{-}O\text{-}Cu]^{+2}$), monomers (e.g., $Cu^{+2}$), or multinuclear clusters (e.g., $Cu_xO_y$). This scope becomes more complex since depending on the Cu/Al and Si/Al ratios, and even the utilized method to synthesise the catalyst, different forms of copper can be obtained, and at different temperatures they seem to be mobile in the cage of the zeolite. In fact, it appears that conventional *in-situ* characterisation methods are not enough to generate a clear explanation. The main part of this PhD thesis is dedicated to fundamental studies regarding Cu-CHA performance in the $NH_3$-SCR chemistry.
During my PhD study, experimental tests have been carried out in order to comprehend the activity of Cu-CHA in comparison to more conventional SCR catalysts, e.g. V-based catalysts. The first part of the study covered Standard SCR experiments over these SCR catalysts. Moreover, a mechanistic study has been carried out, aiming at quantitatively developing and validating a kinetic model for NO oxidation (R.3) on Cu-CHA catalysts, which has been proposed to be very a important step in the SCR chemistry. Firstly, the detailed steps of NO oxidation are proposed and consequently, the rate equation has been derived. Secondly, a systematic set of steady state kinetic runs have been carried out over a commercial Cu-CHA catalyst to address the effects of different operating variables on the rate of NO oxidation. Lastly, the results of these experiments have been employed to estimate the intrinsic rate parameters in the proposed kinetic mechanism. The model predictions were found truthfully in accordance with the experimental results. This mechanistic model seems therefore a step forward towards a better understanding of the SCR-DeNOx activity of Cu-CHA. This NO oxidation model is discussed in the second part of my PhD thesis.

$2NO+O_2 \rightarrow 2NO_2$ **(R.3)**

In the third part of the thesis extensive *operando* spatially and time-resolved XAS measurements have been carried out in order to elucidate the interaction of different species in the SCR reactions.
This work was performed in collaboration with Prof. Jan-Dierk Grunwaldt at the Karlsruhe Institute of Technology (KIT). Various trends have been observed for the $NH_3$ interaction with the active Cu sites on different loadings of Cu-SSZ-13 at low and high temperatures. Such trends supports the idea of two different dominant active sites for $NH_3$-SCR at low and high temperatures. The nature of the active Cu sites in a wide T-range has been studied by detailed XANES and EXAFS analysis.
The integration of the SCR and DPF units (SDPF) in the exhaust aftertreatment system of diesel engines is an innovative solution to decrease diesel engine emissions down to the upcoming regulated levels, which is the topic of the fourth part of my PhD thesis. In this work, the capability of a commercial SDPF, which is a DPF monolithic converter with Cu-CHA coating in the DeNOx activities has been comprehensively studied. Standard and Fast SCR, ammonia oxidation and ammonia TPD experiments have been performed on the sample. Moreover, the effect of aging as a function of time and temperature has been evaluated, employing six aged SDPF samples.
The fifth part of the PhD study is dedicated to another important component of a diesel aftertreatment, i.e. the Diesel Oxidation Catalyst (DOC). As the diesel engines becomes more fuel efficient, the temperature of the tailpipe becomes lower and therefore the cold start emissions turn out to be a more significant problem. In this part of the work, we have focused on the water thermal effect on a commercial DOC in the T-range of engine cold start. The thermal effect of water vapor adsorption on DOC, which causes a strong temperature increase in the DOC monolith, and the impact of the aging process were extensively studied.
Finally, the last part of the PhD work has focused on the production of pure gaseous NO. This study has investigated the feasibility of using a cheap, relatively easy and sustainable process of pure gaseous NO production according to a catalytic reaction well known in Lean DeNOx aftertreatment catalysis. To this end, a $BaO/\gamma\text{-}Al_2O_3$ catalyst was prepared in the laboratory of LCCP and used eventually for further investigations.

# RESPONSIVE LIQUID CRYSTALS (LC), METAL ORGANIC FRAMEWORKS (MOFS), AND BLOCK COPOLYMERS

**Francisco Fernandez**

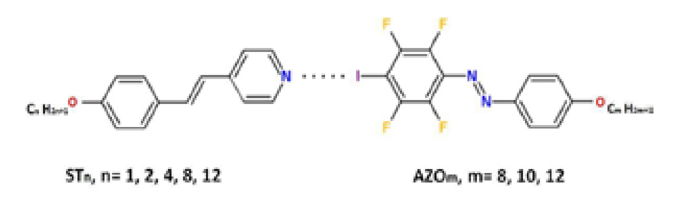
In this Doctoral Thesis, I considered three well known topics in supramolecular chemistry to review the studies developed until now, adding halogen bonding (XB) properties in order to improve their characteristics. These topics are responsive Liquid Crystals (LC), Metal Organic Frameworks (MOFs), and Block copolymers.

## Liquid Crystals

The goal of this work is to show that XB can be used in a very predictable and efficient manner to create photoresponsive LCs with rich photochemical phenomena. It is showed that a rational molecular design, allowed me to prepare a new class of fifteen highly photoresponsive XB-based LCs that display clean and reversible LC-*to*-isotropic and crystal-*to*-isotropic phase transitions in the whole nematic and also smectic phase range and are promising candidates as liquid crystalline actuators.

Dynamic complexes were assembled between three new photoactive alkoxyazobenzene molecule (**AZO***m;*) containing an azo group and five promesogenic stilbazole (**ST***n*) molecules (Fig. 1). None of the starting components considered in this work displayed a LC phase. The strength of our strategy relies on the presence of these alkoxy groups in the XB donor moiety, which allowed us to finely tune the chain length of both components in order to form quite different structures that displayed interesting LC behavior. Particularly, the used fluorinated azobenzene units not only act as efficient XB donors but also possess exceptionally long *cis*-lifetime, allowing us to grow also single crystals of the *cis*-azobenzenes.

The *cis*-state of the studied azobenzenes is particularly interesting, due to the unusually long-measured life-time, equal to 13 days at 20°C. Photoresponsivity has been used to induce an isothermal nematic-*to*-isotropic transition in the supramolecular LC phase. In order to understand the orientation of the molecules in the different phases, birefringence has been measured. The obtained results revealed high values, conceivably related to the good orientation of the LC phase. Illumination of the sample (395 nm) led to nematic-*to*-isotropic transition in about 3 seconds. Furthermore, an observed drop in the birefringence value seemed to indicate the disappearance of the orientational order. The transition has been attributed to the isomerization of the azo molecules from the rod-like form of trans-isomers to the bent form of cis-isomers. The LC phase reappeared within seconds after switching off the irradiation, so a system presenting a completely reversible transition is presented. In addition to these features, our systems undergo a phase transition from the crystalline-*to*-liquid state under irradiation with UV light within *ca.* 30s at temperature below the melting point. Within minutes, the recrystallization occurs through a partial nematic LC phase, and the result is a homogeneous crystalline phase.



1. The complexes prepared in this study are assembled by XB between promesogenic stilbazole molecule (left) and photoresponsive XB donors (right)

## MOFs

A new azobenzene molecule (**1**) has been synthesized. This dye was decorated by dimethylamino group in one ring and two carboxylic groups in para-positions in the other ring with the aim to extend the dimensionality of our coordination system. Using both hydrothermal and isothermal conditions new coordination networks with Zn(II) were obtained. For sake of comparison, we report, also the structure of a closely related network in which the ligand does not have XB donor groups.

I used an hydrothermal synthesis to obtain $\{[Zn(1)(Py)_2](2\text{-propanol})\}_n$ (**3**) that was isolated as red crystals. In the Coordination Polymer, the zinc cation is tetrahedral coordinated by two pyridines and two carboxylate groups forming 1D infinity chains. These chains are linked together by weak halogen bonds I···I to form a 2D structure. The I(1)···I(2) distance is 3.7259(10) Å, C(1)-I(1)···I(2) and I(1)···I(2)-C(2) angles are 160.7(2)° and 115.1(2)°, respectively.

In the MOF $\{[Zn(\mathbf{1})_2(bipy)_2](DMF)_2\}_n$ (**4**), molecule **1**, 4,4′-dipyrdyl and Zinc (II) were assembled in squared planar net forming cavities. Crystallization solvent molecules (dimethylformamide) were encapsulated in the cavities thanks to halogen bonding interaction occuring between iodine atom and oxygen atom of DMF where the distance C-I···O is 2.942(5) Å, and the angle C-I···O is 175.41(11)°. To assess the importance of XB in these frameworks we synthesized **2** which has the same structure as **1** but without iodine atoms. In isothermal conditions and with the same solvent used for the synthesis of **4**, we synthesized $\{[Zn(\mathbf{2})(di(4\text{-}pyridyl)ethylene)](DMF)_{1.81}\}n$ (**5**), and less than two molecules of DMF were found in the cell. However, the solvent does not interact with the surrounding molecules.

Additionally, the photochemistry in diluted solution of our dyes was studied. The UV-Vis spectra of **1** and **2** display an absorption maximum at 400 and 435 nm and their half-lifetimes upon UV-VIS irradiation at 457 nm of the corresponding trans azobenzene, are τ = 3000 s and τ = 850 s respectively.

## Block Copolymers

In this work I show that the selective formation of halogen-bonded domains involving the P4VP blocks facilitates their segregation into patterned structures, even upon casting from a non-block-selective solvent such as chloroform. In addition, I also exploited the reversibility of XBs to remove the small molecule additive by solvent washing, thus resulting in hollow nanotemplates.

The preparation of thin films spin-coated on silicon from the same chloroform solutions resulted in analogous nanostructured patterns. A striking difference was observed between the AFM micrographs of thin PS-*b*-P4VP(DIPFO) and simple PS-*b*-P4VP films. No structuring occurred for pure PS-*b*-P4VP but, conversely, thin films spin-coated from a complex solution under analogous conditions displayed clear microphase separation. Cylindrical P4VP(DIPFO) domains with an average diameter of 27.2 ± 5.7 nm were observed, embedded in a PS matrix with an average center-to-center distance of 45.3 ± 5.8 nm. Indeed these nanostructures were mostly arranged in a hexagonal pattern, although domains with tetragonal order were also present. We point out that the addition of DIPFO, which is highly soluble in chloroform, is not expected to raise the solvent's block selectivity. Taken together, these observations point at a crucial role played by XB to achieve efficient and immediate microphase separation upon spin-coating of our films, without any need for subsequent annealing treatment. The presence of XB in the spin-coated films was confirmed by the red shifts of the C−F stretching modes originally located at 1112 and 1090 $cm^{-1}$ in pure DIPFO.

The reversible nature of XB allowed also the removal of DIPFO by ethanol washing, following an analogous concept previously illustrated for hydrogen bonded polymeric systems. The complete removal of the fluorinated additive was proven by the disappearance of FTIR absorption bands. Conversely, the structural organization of the PS polymer matrix was unaffected by the washing.

The presence of hollow spaces in the cylindrical structures was further proved by metallation experiments in which gold, was evaporated and deposited on top of an ethanol-washed thin complex film, followed by washing with acetone to remove the polymer template. The procedure resulted in gold nanostructures with a height of about 3-4 nm and a rather broad size distribution, proving that DIPFO can be removed from the thin complex films to yield hollow structures with potential use as nanotemplates.

# ENZYMATIC-SENSORS FOR MICROBIAL FUEL CELLS: FROM BIOELECTROCHEMICAL MECHANISMS TO ELECTRODES DEVELOPMENT

**Matteo Grattieri** - Supervisor: Prof. Massimiliano Bestetti

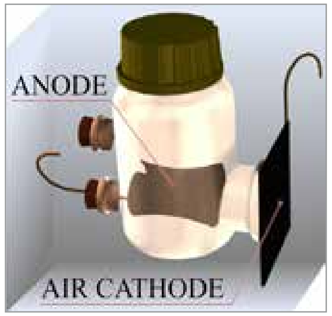
Microbial fuel cell (MFC) has been one of the most attractive biotechnology in the recent years since it was demonstrated that it can perform the degradation of organic matter with the concomitant production of electricity. The possible applications of the technology range from the self-powered wastewater treatment, self-powered sensors, production of electricity for small devices in remote regions and heavy metals recovery. This technology presents several issues and drawbacks, from fundamental to practical, which still limit the scale-up and the industrial application.

Single-chamber MFC (SCMFC) is a particular configuration that consists of a unique compartment where anode and cathode electrodes are exposed to the same solution, no polymeric membrane is placed between the two electrodes and protons produced at the anode can freely diffuse toward the cathode. This configuration is known as "air-cathode" MFC since one side of the cathode is directly exposed to the air while the other side is facing the same solution of the anode.

The absence of a physical barrier between the electrodes of SCMFC brings colonization of the cathode by bacteria, obtaining a bio-catalyzed electrode. However, the absence of the barrier could theoretically increase the oxygen diffusion toward the anode, decreasing the columbic efficiency and the power production performances. There is a lack of studies related to the oxygen consumption in Single Chamber Microbial Fuel Cells, although the knowledge of bioelectrochemical mechanism occurring at the cathode is of primary importance for the operation of the device.

Open-Air Cathodes are made with polytetrafluoroethylene (PTFE) on the air-side of the electrode, to avoid solution leakage. Thus, PTFE role on the oxygen reduction reaction (ORR) that takes place at the cathode should be considered. However, no detailed studies on its influence on the ORR performances are present in literature.

The application of enzymatic cathodes could improve the open circuit potential (*ocp)* and power production of SCMFC, but has to deal with enzyme inhibition due to the direct contact of the enzyme and the electrolyte of the anodic chamber, wastewater and several different ions that can bind to the actives sites of the enzyme, decreasing the amount of sites available to the substrates.



1. Schematic Representation of a Single Chamber MFC.

A possible application of stainless steel as support for biocatalyzed anodes, to decrease the cost of SCMFC (AISI304 is a couple of orders of magnitude cheaper than carbon cloth), has to deal with microbial influenced corrosion.

Considering the above remarked issues, the research activity had both fundamental and practical goals and the research project has been focused to four main objectives.

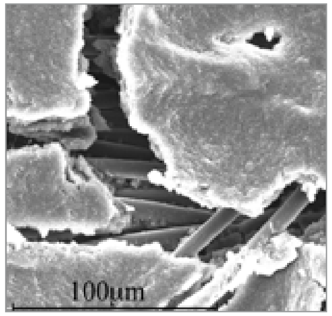
The first objective was the study of the bioelectrochemical mechanism of oxygen consumption in Single Chamber Microbial Fuel Cells. A hand-made amperometric Direct Electron Transfer enzymatic sensor based on bilirubin oxidase was developed and applied in SCMFC to study the oxygen content. Prior to the application in SCMFC, the enzymatic sensor was calibrated in phosphate buffer and wastewater, in different aeration conditions. The lifetime of the biosensor was studied by calibrating the same sensor along 14 days and evaluating the loss in current response.

The hand-made enzymatic microsensor allowed clarifying the bioelectrochemical mechanism of oxygen consumption in SCMFC.

The cathodic biofilm developed on the open-air cathode plays a key role to maintain the anaerobic condition in the anode chamber. The biofilm acts as "natural barrier" for the oxygen diffusion to the anode.

The second objective was the study of the PTFE effect on the oxygen reduction reaction in open-air biocathodes. Four sets of SCMFCs were built, where the difference was in the composition of the external layer of the cathode (GDL), with PTFE content from 60 to 200% w/w (weight ratio is referred to the carbon powder).

The effect of PTFE content in the cathodes of operating SCMFCs on ORR was evaluated by electrocatalysis parameters. The results show that SCMFCs with the lower PTFE percentages in the GDL had a prompt startup and high current outputs. Electro-activation of the cathodes was shown by a change of the Tafel slope from 120 mV/decade of current (corresponding to no electrocatalysis), down to a lower limit of around 80 mV/decade of current (electrocatalytic behavior). Activation is reversible, related to the biological consumption of acetate in the SCMFCs. The ORR seems mostly related to biologically-assisted electron transfer activation, inhibited by the PTFE presence in the triple-contact zone.



2. SEM micrograph of a 60% w/w PTFE cathode, GDL side, after three days of operation.

To further improve the electrocatalytic performance of the biocathode, enzyme electrode has to be developed. Thus, the third objective was the study of the $H_2O_2$ inhibition on laccase-based enzymatic biocathodes in mediated electron transfer (MET) and direct electron transfer (DET) configuration. The MET laccase-biocathode was made using Osmium Polyallil(amine) as redox mediator. The DET laccase-biocathode was made by adsorption of the enzyme on modified gold electrode with Carbon Vulcan®.

The study of $H_2O_2$ inhibition remarked two different mechanisms depending on the wiring technique utilized for the sensor development. The inhibitor binds to the free enzyme or the enzyme-substrate complex, obtaining a non-competitive reversible inhibition for the MET biocathode. The inhibitor binds preferentially to the enzyme-substrate complex in the case of the DET biocathode, obtaining an uncompetitive inhibition, especially at high $H_2O_2$ concentration.

The fourth and last objective was the study of the electrochemical behavior of AISI304 applied as anode electrode in SCMFC. The suitability of AISI304 as anode support was investigated in different aeration conditions. AISI304 anode suffered the pitting corrosion with the presence of residual oxygen in the anode chamber. Whereas, if strictly anaerobic conditions were ensured at the electrode surface, microbial corrosion did not occur. AISI304 and carbon cloth showed similarity in term of power generation, organic substances oxidation kinetics and dependence of the electrocatalytic properties on the biofilm settlement and stability.

# RECOVERY OF RARE EARTHS AND PRECIOUS METALS FROM WEEE (WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT) BY ACID LEACHING AND IMMOBILIZED AGENTS

**Elena Maria Iannicelli Zubiani** - Supervisor: Prof. Cinzia Cristiani

Tutor: Prof. Tiziano Faravelli

Today there is an increasing need for rare earths (REs) due to their usage in numerous high-technology applications such as: optical, electronics, ceramics and nuclear. Currently each EU citizen produces about 17 kg of waste electrical and electronic equipment (WEEE) per year. These wastes are rich in precious and strategic metals and, in many cases, are characterized by higher REs contents than those of natural minerals. Accordingly, recycling can be considered a valuable opportunity: this perspective is known as “urban mining”. For these reasons, the study of an efficient REs recovery from WEEE can lead to undeniable socio-economic and environmental benefits.

The present work performed under the project “E-WASTE - Il ciclo intelligente” (ID 40511448, financed by Lombardia Region) focused on the recovery of REs and precious metals from WEEE, namely magnetic components, mobile phones and Printed Circuits Boards (PCBs). In particular one of the final aim of E-WASTE project was the realization of a pilot plant for WEEE treatment carried out through the partnership of two large companies (Amsa and Stena), a medium-sized enterprise (Consorzio Remedia), three SMEs (Seval, Tecnochimica, and, Gaser), two research organizations (Politecnico di Milano and Cefriel) and two public administrations (Comune di Milano e Comune di San Donato Milanese). During the PhD activity the plant was designed and projected with the industrial partners, basing on experience, known processes and research activity. Different unit operations are quite well known, while some steps are completely innovative. The research activity deeply described in the present work was focused on the study of innovative processes aiming to the REs recovery from WEEE.

From a technological point of view, recycling of end-of-life WEEE and recovering of metals therein contained can be divided into three major steps: disassembly, upgrading and refining. For the last step, different methods have been proposed. In particular, hydrometallurgical method has been reported as one of the most interesting because it is generally applicable to very different compositions and allows the same processing steps of the REs extraction from primary ores. On the other hand, some disadvantages of this process are: the number of process steps, the consumption of large amounts of chemicals and the generation of huge amounts of waste water. Some of the reported disadvantages are related to the step of metal ions removal from aqueous solution. Recently, the adsorption method is obtaining more and more attention because of its advantages with respect to liquid-liquid extraction such as: high recovery efficiency, short extraction time, high enrichment factor, low cost, and low consumption of organic solvents.

In particular, the use of clays and activated carbon as solid-phase has some outstanding advantages, such as low cost, good mechanical properties, good acid tolerance, convenient solid-liquid separation and excellent reusability. The present research activity has been focused on the investigation of these solid sorbents, evaluating different solid matrices and different suitable modifications with the final aim of removing the metal ions and of recovering them if they have high added value.

The experimental activity was divided in two main parts. The first one concerns the study and the comprehension of the interaction mechanisms. Since the involved systems are indeed very complex (e.g. in a magnet from a hard-disk there are 16 different ions and the amount of REs is very low), the study was carried out on model systems. The second part is mainly focused on the industrial application: different parameters (as the reusability of the solids, as the complexity of real solutions and as preliminary reasoning about the sustainability of the global process) are considered.

As a first step, two natural smectite mineral clays (STx and SWy) were studied for lanthanum (chosen as representing element of REs family) adsorption and release in order to: 1) verify the clays sorption capability, 2) investigate the sorption mechanisms and 3) optimize the experimental parameters, such as contact time and pH. Since the global efficiencies of lanthanum recovery were around 30-35%, modified clays were also synthesized by intercalating different polyamines having coordinating properties. N-(methoxy-polyethylene glycol) ethylene diamine showed an improvement in the global efficiency (43%). Its intercalation mechanism was deeply investigated, varying operating parameters such as polymer concentration and pH. Optimal intercalation conditions for lanthanum recovery purpose were: 90 mM of initial polymer concentration and pH of about 11, corresponding to a not-protonated condition of the coordinating amine groups. In order to further increase the global efficiency of the process, different polyamines were tested in these optimal conditions. In particular two linear ethylene amines with different length of chain, a branched ethylene amine and an ethylenediiminodipropylamine were intercalated in the clay STx. In every case the adsorption and release behaviours towards lanthanum were studied. The results obtained with these polyamines pointed out huge increase in the lanthanum recovery global efficiency, achieving values around 85% (99.9% in uptake, 84% in release).

Then a different solid matrix was considered: activated carbon was tested as sorbent material. The mechanism mainly involves surface adsorption, allowing lanthanum recovery efficiencies around 50%. Also in this case the modification of the solid with a linear ethylene amine leads to a huge increase in the lanthanum recovery global efficiency, achieving values around 90% (99.9% in uptake, 90% in release).

The adsorbed and released metal ions were calculated by ICP-OES while the amounts of intercalated polyamines were estimated by COD analysis of the residual amounts in solution and deduced by difference. All the solid materials were characterized by FT-IR, DTA-TG and XRD. In addition, pristine clays have been also investigated by XPS measurements.

The second main part of the present work focused on the final application; the reusability of the evaluated sorbent materials was first studied, proposing a regenerating system able to work for at least four recovery cycles. Then more complex (lanthanum and copper, lanthanum and nickel) and real solutions coming from different leached electronic scraps (mainly hard disk magnet and mobile phones) were tested for adsorption onto the studied materials. The obtained results (80% in uptake and release to be optimized) are the basis for the implementation of the pilot plant by December 2015, where the solid sorbents work as purifying materials with the perspective of recovering.

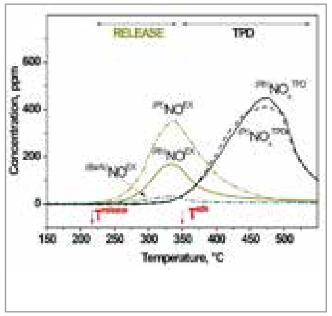
A preliminary analysis about the sustainability of the global WEEE treatment was also carried out showing the great environmental benefits of the proposed process.

# MECHANISTIC INVESTIGATION OF NO$_X$ STORAGE REDUCTION (NSR) OVER PT- AND RH-BASED BAO/AL$_2$O$_3$ CATALYSTS

**Lukasz Kubiak** - Supervisor: Prof. Luca Lietti

Tutor: Prof. Elisabetta Brenna

The removal of nitrogen oxides from diesel engines based on the NO$_x$ Storage Reduction (NSR) concept is an appealing solution to successfully control exhaust emissions for lean burn engines, i.e. operating under high air/fuel ratio. In this technique NO$_x$ are stored on the catalyst surface during the normal engine operation; then the engine is made running rich for a short period of time and reduction of the stored NO$_x$ is attained. Typical catalytic materials comprise noble metals like Pt, Pd, Rh and storage elements (Ba, K) dispersed over a high surface area carrier (e.g. alumina). This thesis work addresses mechanistic aspects and reactivity of NSR catalysts. In particular, catalysts with different noble metals (Pt, Rh) have been considered to better enlighten the role of the noble metal on the catalyst reactivity (adsorption of NO$_x$ and reduction). Particular emphasis has been given to the analysis of the reduction phase; for this purpose different reductants have been used (H$_2$, NH$_3$, n-heptane) and aspects related to the formation of N$_2$O, a highly undesired by-product, have been deepened. Concerning the influence of nature of the noble metal (Pt vs. Rh) on the NO$_x$ storage-reduction, it was found that the storage of NO$_x$ is affected by the oxidizing properties of the noble metal (with Pt being more active than Rh) and by the metal dispersion. Also the reduction of the stored NO$_x$ is affected by the nature of the noble metal, with Pt being more active than the Rh counterpart. Isotopic labelling studies showed that the reduction implies the release of NO followed by its reduction; the NO release is a redox reaction catalysed by the noble metal since on bare Ba/Al$_2$O$_3$ the process does not occur.



1.

Figure 1 compares the NO release from nitrates (measured by isotopic exchange of nitrates with labelled NO) and the thermal decomposition of nitrates (TPD) over Pt- and Rh-based catalysts. It is noted that both the exchange (release) of NO and the thermal decomposition of nitrates are not affected by the nature of the noble metal since similar onset temperatures ($T^{RELEASE}$ and $T^{ADS}$, respectively) have been observed for both Pt- and Rh-based sanples (Figure 1). Notably, NO release does not involve the thermal decomposition as a preliminary step (Figure 1, compare $T^{RELEASE}$ vs $T^{ADS}$), being $T^{RELEASE}$ lower than $T^{ADS}$.

The release of NO is favoured by the presence of reductant species, since the reduction of the stored NO$_x$ is observed at lower temperatures than the NO$_x$ release. The presence of reductants lead to the reduction of the noble metal, and this favours the NO release process. In this respect, Pt is more easily reducible than Rh, and this leads to the superior reactivity of Pt vs. Rh during the reduction of the stored NO$_x$.

Concerning the reduction of the stored NO$_x$, mechanistic aspects have been deepened over the Pt-containing sample. In particular, the reactivity of hydrocarbons (*n*-heptane) has been investigated, that is not fully understood so far. It is found that n-heptane is an effective reductant of both gaseous NO and stored NO$_x$.

The reduction leads to the selective formation of N$_2$ at higher temperatures, whereas significant amounts of N$_2$O are also formed at lower temperatures. On the basis in-situ FT-IR analysis, it has been found that under the investigated conditions the reduction of gaseous NO or stored NO$_x$ does not involve the formation of surface isocyanates/cyanates (NCO/OCN) species, or partially oxygenated carbon containing compounds like aldehydes (R-CHO). This contrasts with literature data showing the formation of surface NCO groups, although when using short chain unsaturated hydrocarbons (e.g. C$_3$H$_6$) in the reaction.

The reactivity of n-heptane in the reduction of various NO$_x$ species (gaseous NO, nitrates, nitrites) is not markedly affected by the presence of water, despite the fact that in the presence of water the hydrocarbon molecules are in involved in the Steam Reforming (SR) reaction. In fact the SR reaction occurs to a very limited extent in the temperature range where the reduction of NO$_x$ species is active. Therefore it is likely that n-heptane directly participates in the reduction of the stored NO$_x$: it is expected that the Pt sites are kept in reduced state by the hydrocarbon, which invokes the migration of stored NO$_x$ toward active metal sites followed by dissociation into N- and O-ad-atoms. Then O- ad-atoms are scavenged by the hydrocarbon, while N ad-atoms and NO ad-species recombine to generate the main products of reaction, i.e. N$_2$ and N$_2$O.

Finally, concerning N$_2$O formation, mechanistic aspects regarding the formation of N$_2$O over Pt and Rh- based NSR catalyst clearly shows that N$_2$O formation involves the presence of gas phase NO. Notably N$_2$O formation originates from the coupling of undissociated NO molecules with N-adspecies formed upon NO dissociation on the redox centers provided by PGM sites. Accordingly, partially reduced PGM sites are required to catalyse the NO dissociation into N- and O-adspecies on one side, but to prevent complete NO dissociation on the other side. This process may proceed even in the absence of a reductant, provided that reduced PGM sites are initially present, since O-adatoms originating upon NO decomposition are involved in the formation of nitrite species according to O-assisted disproportionation reaction of NO (reactions (1)-(3)), to give the overall reaction (4).

$$NO + 2\,Me \rightarrow Me\text{-}N + Me\text{-}O \quad (1)$$

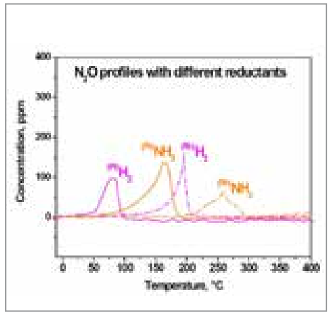
$$NO + Me\text{-}N \rightarrow N_2O + Me \quad (2)$$

$$2\,NO + Me\text{-}O + O^{=} \rightarrow Me + 2\,NO_2^- \quad (3)$$

$$4\,NO + O^{=} \rightarrow N_2O + 2\,NO_2^- \quad (4)$$

where Me is Pt or Rh supported on BaO/Al$_2$O$_3$ and O$^=$ is lattice oxygen of BaO site

The formation of N$_2$O is favoured at low temperatures, when PGM centers are being reduced, and is prevented at higher temperatures when redox sites are in reduced state and complete dissociation occurs. N$_2$O is observed at lower temperature in the reaction with H$_2$, if compared to NH$_3$, as shown in Figure 2. These results are in line with higher reduction capacity of H$_2$ in the scavenging of O- adatoms from the PGM sites; in particular of Pt containing catalyst due better redox properties with respect to Rh based catalytic samples.



2.

# MODELLING OF FOOD THERMAL PROCESSES TOWARDS QUALITY AND ENERGY OPTIMIZATION

**Davide Papasidero** - Supervisor: Flavio Manenti

Recently, many researchers are focusing their attention to food process modeling as a tool for optimizing not only the energetic and economic aspects, but also the final product texture, flavor and nutritional value. Modeling is also a valid instrument for better understanding the different scales of the cooking process.

Quantitative models can be used for many activities and applications. A computational model of food processes is a computer tool that can make predictions of growth and inactivation kinetics, or predict dynamics over a food chain.

It is extremely important to underline that food is usually very far from an ideal system: both experimental techniques and models used for homogeneous systems, as well as those for heterogeneous ones with two or three phases for many chemical systems could be useless for most of the practical applications. This leads to models simplification and multi-scale simulations with a hierarchy of interconnected sub-models, where homogenization is almost mandatory for reasonable process viewpoints. Bread Baking is one of the clearest example of food process that involves several chemical and physical phenomena. For this reason, the study of this process has been for decades to the attention of several researchers, that focuses on the general problem or to specific issues, such as for example the flavor generation, the browning development, the water and heat transport, the influence on oven design (e.g. for CFD based design), the volume expansion, etc. An important issue with cooking (and baking) processes is that they are usually batch processes, and dynamic models are recommended for their description. In addition, some key assumptions can be required to make a simulation fast enough, certainly going to the detriment of the details but getting reasonable results, when compared to the aim of the research. Furthermore, when searching for food material literature, one has to face the problem of the specificity of a single food. Often, the experiments for its validation and for the properties and coefficients derivation, as well as for the boundary conditions, are designed on a very specific foodstuff and experiments, and a general approach requires new assumptions and/or experimental tests to be applied to the specific case. By the way, a general approach is still possible, being careful to develop and use equations based on general phenomena, eventually applied to the specific context by modifying some terms and by introducing some parameters. Within this context, a general model based on heat and mass transport equations has been developed and applied to bread baking, then further extended to two other food kinds, meat roast and multicomponent frozen food.

The model needed a proper dissertation on phase transitions, with particular reference to water boiling and ice melting. One appropriate phase change formulation have been introduced and implemented in a commercial finite element method software through suitable mathematical functions, to overcome the numerical difficulties related to stiff differential equations. A multiphase, multicomponent matrix has been chosen to flexibly represent different food matrices, with transport properties coming from this approach. All the models have been validated with experimental data.

One other interesting application of the food models can be the optimization for specific targets, dealing with either quality or sustainability aspects. The energy target is relevant since commercial electric ovens are part of the domestic equipment that requires a huge amount of energy to pursue the food transformation, using few technologies such as forced hot air convection, irradiation and, sometimes, microwaves. Dynamic optimization techniques have been applied to bread baking using the developed model, through the assessment of the energy demand of bread to be cooked. Energy is provided to the food load due to a combination of energy sources. In the case study, forced air convection and irradiation were responsible for the bread baking. The related dynamic optimization procedure included the possibility to select optimal temperatures in discrete time steps. The optimization has been subject to selected quality constraints, related to the crumb starch gelatinization degree (as a minimum requirement for "cooked" bread) and crust browning (with a range of consumer acceptability). The optimization led to a 20% energy saving compared to a base baking case with constant oven temperature. It also suggested to supply most of the energy in the first part of the process (heating), when browning phenomena are less relevant (at lower temperature) and a decrease of process temperatures in the final part, to limit the temperature increase affecting the browning reactions.

One another relevant topic is the production of aroma and color compounds. Heat and mass transfer and moisture loss influence chemical reactions such as starch gelatinization, sugar caramelization, lycopene degradation and Maillard reaction. This condition flavor and texture development, color change.

Flavor and odor are fundamental characteristics of food, since they strongly affect the global quality and the consumer sensorial perception. For this reason, it is interesting to analyze the volatile profile and the possibility to predict its development based on initial formulation and cooking process. Bread baking is a possible application case for this analysis. Maillard reaction is probably the most important related phenomena, resulting from the interaction of proteins and reducing sugars and from the subsequent chain of reactions. Despite a considerable amount of literature on the produced compounds, one can find just few sources on the kinetics of the main involved compounds.

In addition, most of the kinetic models are developed based on model systems, i.e. homogeneous systems where few compounds are loaded in a solution (e.g. with glycerol) to react in isothermal conditions, while real food matrices are rarely considered.

For this reason, either lumped models for the description of compound classes can be introduced with more or less success for the description of flavor and color, or a variety of complex analytic techniques are needed to get partial results for a specific food matrix (e.g. French fries, biscuits) in simple operating conditions (e.g. isothermal). Even in this case, the kinetic parameters have a very high uncertainty. The latter situation still represents a rarity in the food chemistry field, and only few papers have been published on the subject, avoiding the dependency on the local temperature, water content and activity, pH and structure, which could be derived from complex crossed analyses and coupled heat and mass transfer model.

Within this context, a series of experiments with a domestic oven equipped with a PTR-TOF-MS have been performed on bread baking tests to identify the dynamic production of aroma compounds and related intermediate compounds selected on literature studies. For each experiment the mass spectrometer detected 355 different compounds, with concentrations ranging from 0 to approximately 700 ppbv, with variations measured in the order of 0.001 ppbv, with a resolution on masses of 0.0001 amu. A simplified physical model have been coupled with a kinetic model based on specific aroma markers production path to develop a tool for the prediction of aroma production from tests performed in analogous conditions. This approach can be further detailed based on more information on the chemical state of the food matrix, and more and more mechanisms could be identified with powerful analytical and computational devices. This strategy aims at the quality parameters optimization through the combined use of sensory and analytical measurements with models and algorithm, to be used both for the small scale cooking devices and for the industrial-scale food processing.

# AMINO- AND GUANIDINOGLYCOSIDE-BASED VECTORS FOR GENE AND DRUG DELIVERY

**Aurora Sganappa**

The overall goal of the project of this thesis was the use of aminoglycosides for 1) the development of new multifunctional gene delivery vectors, 2) the development of new multivalent carriers for drug delivery and 3) the synthesis of a collection of new antibiotics. In recent years new non-viral vectors for gene and drug delivery have become more and more important in order to overcome the use of viral vectors, due to their potential dangerous drawbacks, and facilitate drug entery into cells. In this experimental work, different kind of non-viral vectors for gene delivery studies were synthesized, using dendrimeric, lipidic and hybrid lipidic-dendrimeric cationic systems grafted with aminoglycosides. Aminoglycosides are a large family of well-studied potent antibiotics. Therefore, new potential dendrimer- and lipidic-aminoglycoside conjugates were synthesized, fully characterized and tested for their ability as transfectants and their cytotoxicity. PAMAMG4-aminoglycoside conjugates were extensively studied and were identified as one of the best multifuncional non-viral vectors having optimum transfection efficiency, low cytotoxicity and good antibacterial activity. Cationic lipid vectors as calix[4]arene-aminoglycoside conjugates and hybrid lipo-dendrimer(n)-neomycin conjugates were synthesized, characterized, and investigated as potential multifunctional carriers. Preliminary results evidenced a good ability as tansfectants and a very low cytotoxicity, making them really applicable in gene delivery field. Guanidinoglycosides, derivatives of aminoglycosides obtained by total substitution of amino groups with guanidinium groups, have showed their great ability to promote the cellular uptake of high molecular cargos (i.e. therapeutics molecule) at namolar concentration in a heparan sulphare dependent way. We have thus used these guanidinoglycosides to graft PAMAM dendrimers obtaining new multifunctional conjugates with future applications in drug delivery field. Studies on these conjugates have shown their high cellular uptake in heparan sulphate dependent way at nM concentrations, with different mechanism of internalization.  Finally, the chemistry of aminoglycosides was investigated in an innovative multicomponent domino process recently developed in our laboratories. MC reactions were not commonly used until now with aminoglicosides due to the large number of functional groups on their structure. Neverteless, this new multicomponent domino process was used to synthesize sugar-neomycin conjugates in good yields, as novel antibiotics. MICs studied have disclosed their good antibacterial activity against *MRSE* and *E.Coli* bacteria.