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DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

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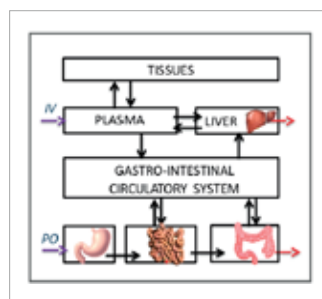
Department of Energy

Alessandra Beretta, Luca Lietti, Matteo Maestri, Isabella Nova, Enrico Tronconi.

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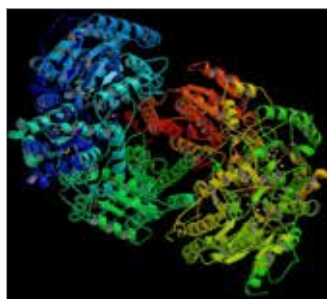
**Structure simulation of Nitrogenase enzyme for N_2 conversion to NH_3**

Compartmental structure of the PBPK model. Model inputs are the drug administration modalities (blue arrows, IV = IntraVenous, PO = Per Os, or Oral). Boxes are the model compartments and represent specific organs/tissues

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.**

The general topic for the doctoral program in Industrial Chemistry and Chemical Engineering is the application
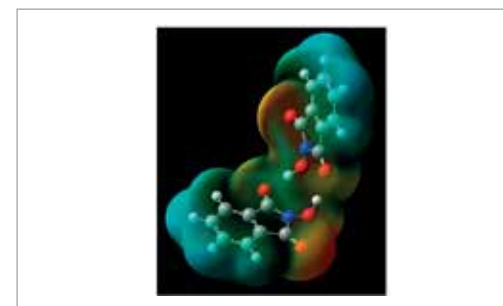

Theoretical structure and relative electrostatic potential surface (ESP) for the most stable dimer of NHPI (1), calculated in gas phase at 298 K at B3LYP/6- 311+G(d,p) level of theory

Materials and Chemical Engineering (DCMC) and the Department of Energy (DENG).

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 responsibility of the organization and of the contents of the doctoral program is attributed to the Professors
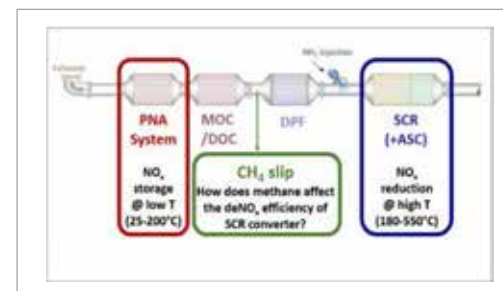
The NOx emission control strategies and issues in an exhaust aftertreatment system for lean-burn vehicles

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). Research activities span across the nano/micro scale up to the macro scale. Thus, 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 candidate may work with research groups at both the Department of Chemistry,
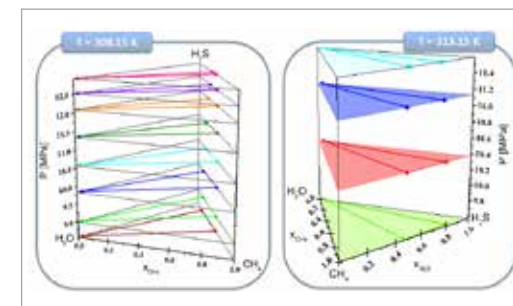
VLE and VLLE measurements for the system CH_4-H_2S-H_2O.

Committee (PC), which is composed by highly qualified and active researchers belonging to Chemistry, Materials and Chemical Engineering (CMIC) and Energy (DENG) Departments.

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.

Hazardous gas dispersion simulation from an industrial accident

DESIGN AND PREPARATION OF COMPLEX NANOSTRUCTURES AIMED AT BIOMEDICAL APPLICATIONS

Chiara Bongio - Supervisor: Elena Vismara

The purpose of this PhD project was the preparation of a composite nanoscale biomaterial based on the assembly between iron oxide nanoparticles and glycosaminoglycans (GAG), capable to combine therapeutic and diagnostic imaging aid functions (**Figure 1**). Indeed, while Super Paramagnetic Iron Oxide Nanoparticles (Fe_3O_4, SPIONs) are feasible as MRI negative contrast agents, the organic counterpart composed by Hyaluronic acid or Heparins derivatives benefits from active-targeting and/or antimetastatic activities. The further presence of Bovine Serum Albumin (BSA) plays an additional role within the described nanocarrier by increasing the biocompatibility and providing handles for hydrophobic cytotoxic drugs (such as Paclitaxel, PTX). At first, all the cited biomolecules were chemically coupled with dopamine (DA) and then chelated to inorganic cores of SPIONs by means of the enediol of DA itself.

Hyaluronic Acid (HA) based SPIONs (Fe_3O_4@BSA/HA) appear as nanosystems of 70–90 nm size containing different iron cores of 5 nm, quite homogenous and capable to afford well-dispersed and stable colloid. They show a good potential in terms of drug loading, by improving PTX water solubility by at least four orders of magnitude. Furthermore, Time Domain-NMR experiments highlight their very good capacity to interfere with relaxation times of surrounding water protons (prerequisite for the applicability as negative contrast agents).

The functionalization of SPIONs with Heparin derivatives (Low Molecular Weight and glycol-split Heparins) gave results consistent with the ones obtained with HA-SPIONs, in particular regarding r_2/r_1 ratios of SPIONs@BSA/LMWH and SPIONs@BSA/gsUFH comparable to those of SPIONs already in the market. Unfortunately, some cytotoxicity problems were encountered.

The solution of encountered cytotoxic issue paved the way to an innovative formulation strategy which takes advantage of the encapsulation of heparin-based SPIONs within Self-Assembled Lipid Nanoparticles (SALNs), generally considered biocompatible. SALNs are efficient carriers for Fe_3O_4@hepa, reducing their cytoxicity to CaCo-2 cells and overcoming the loss of electrostatically linked heparin coating in biological fluids. SALNs– Fe_3O_4@hepa are efficiently internalized in CaCo-2 cells, thus being a promising tool for the delivery of engineered Fe_3O_4@hepa to lymphatic circulation by the oral route.
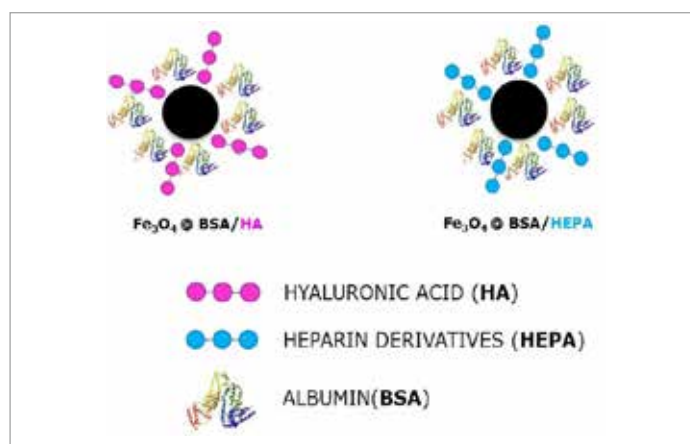

Fig. 1 - Schematic representation of Fe_3O_4 nanoparticles functionalized with glycosaminoglycans and albumin.

FIRST PRINCIPLES MODELING OF STRUCTURE AND ACTIVITY OF NANOPARTICLE CATALYSTS UNDER REACTION CONDITIONS FOR STRUCTURE-DEPENDENT MICROKINETIC ANALYSES

Raffaele Cheula - Supervisor: Matteo Maestri

There is no doubt that the rational interpretation of the relationships between the structure and the activity in heterogeneous catalysis is a crucial task in the quest of engineering the chemical transformation at the molecular level. In this respect, multiscale analyses based on structure-dependent microkinetic modeling is acknowledged to be an essential key-tool to achieve a mechanistic understanding of the catalyst functionality. However, the effect of the structure of the catalyst on reactivity and selectivity is at present neglected in state-of-the-art microkinetic modeling with predictive character. As such, a "material gap" hinders the analysis of the underlying mechanisms at the atomic-scale level. To fill this gap, the modeling of the catalyst structure under reaction conditions is required (Figure 1). Moreover, the modeling of catalytic processes from first principles usually focuses on the study of the catalyst structure and of the reaction rates at the catalyst surfaces as separate phenomena. However, structure and catalytic activity of nanoparticle catalysts are strictly correlated, and they mutually influence each other. Therefore, in the aim of gaining a fundamental understanding of the relationships between the structure and the activity from first principles, new methodologies for the concerted simulation of the structure and the activity of the catalyst materials must

be developed. This is considered an urgent and ground-breaking task both in the fundamental science and in the intensification and development of new and improved catalytic processes. Indeed, it would represent a major step forward in the multiscale modeling with an interdisciplinary impact and it would pave the way toward the nano-design of activity and selectivity.

This thesis presents the development and the application of methodologies for the analysis of the relationships between structure and activity in heterogeneous catalysis from first principles electronic structure calculations. The methodologies are based on the combination of microkinetic modeling and *ab initio* thermodynamics with Wulff constructions and Boltzmann

statistics at given conditions of chemical potential in the reactor. *Ab initio* thermodynamics is applied to characterize the bulk and surface structure of the catalyst. The three-dimensional shape of catalyst nanoparticles and the corresponding distribution of active sites are calculated either with the Wulff construction method or Boltzmann statistics, especially at low nanoparticle sizes, where a statistical representation of the catalyst morphology is needed. In doing so, the structure and the composition of the atoms at the surface is determined, and therefore the "*nature*" of the sites in reaction conditions is fully characterized. Then, microkinetic analyses are performed on the different sites to unravel the "*identity*" of the dominant

active site in reaction, i.e., the sites that give a major contribution to the overall reaction rate. In this thesis, a structure-dependent microkinetic model is developed, which consists in the concerted simulation of the desired chemical reaction path at the catalyst surface along with the morphological transformation of the catalyst induced by the variation of the reaction environment, needed for the identification of the "*nature*" and the "*identity*" of the active sites of the catalyst (Figure 2).

The methodologies developed are applied for the study of industrially relevant catalytic systems. The study of the CH_4 catalytic partial oxidation (CPO) on Rh enables to interpret experimental evidence

that show a change of reaction selectivity induced by a drastic morphological transformation of the catalyst occurring during reaction. The application of the methodologies to the water-gas shift reaction (WGS) on Rh allows for the rational interpretation of kinetic experiments, which show two distinct reaction mechanisms for the direct and reverse direction of the reaction. The quantification of metastable nanoparticles in equilibrium with the thermodynamically favored ground state shape of the catalyst is particularly relevant for nanoparticles samples with low dimensions, which are influenced by particle size effects. In this thesis, the modeling of such metastable structures is achieved

through the application of Boltzmann statistics and the successive analysis of the resulting ensemble average of nanoparticle shapes. The application of such a methodology on Rh nanoparticles under methanation reaction conditions enables to unravel the importance of metastable particles for the reaction rate of the important CO dissociation step. Eventually, the methodologies described in this thesis are applied for the interpretation of experimental observations of NiO particle growth in molten alkali salts media. Such analysis allows to identify the agents responsible for the formation of high-index facets, which are particularly suitable for partial oxidation applications.

As a whole, this thesis provides an effective pathway to unraveling the "*nature*" and the "*identity*" of the active sites under reaction conditions, and it represents a very important step to explicitly introduce the effect of catalyst structure in the microkinetic analysis of heterogeneous catalytic processes.
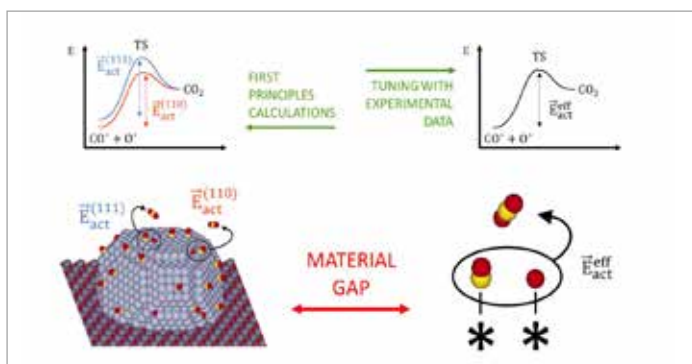

Fig. 1 - Structureless microkinetic models in heterogeneous catalysis rely on simplified assumptions and on the tuning with experimental data. The inclusion of first principles calculations in multiscale modelling of heterogeneous catalysis requires the knowledge of the catalyst structure in reaction conditions and can provide fundamental insights on the relationship between structure and the activity.
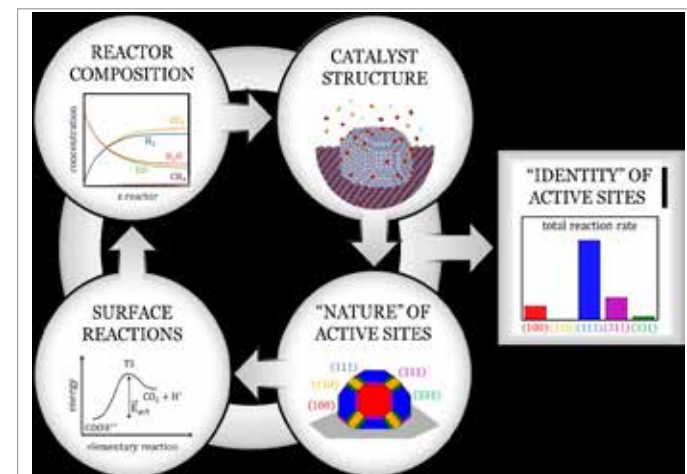

Fig. 2 - Scheme of a structure-dependent microkinetic model, which describes the structure of the catalyst and its catalytic activity (surface reactions), for the identification of the "nature" and the "identity" of the active sites.

LOW TEMPERATURE ISSUES OF SCR SYSTEMS: FROM FUNDAMENTAL UNDERSTANDING OF THE STANDARD SCR REACTION MECHANISM TO PRACTICAL APPLICATIONS FOR COLD START EMISSIONS CONTROL

Federica Gramigni - Supervisor: Enrico Tronconi

Controlling NOx emissions from combustion engines is one of the most important issues for air quality management, as these species are detrimental for the human health and the environment. In this context, the development of exhaust gas aftertreatment devices plays a key role to meet government regulations. Currently, NOx emissions from diesel vehicles are efficiently reduced in warm engine conditions by ammonia/urea over NH_3-SCR catalysts (e.g. Cu- or Fe- exchanged zeolites). On the contrary, the amount of NOx released in the atmosphere is significantly higher during the cold start phase. Indeed, during this transient: i) the inability of decomposing urea prevents from fully exploiting the SCR technology; ii) Cu- and even more Fe-zeolites have a poor deNOx activity. Moreover, a complete fundamental understanding of the Standard SCR reaction ($4 NO + 4 NH_3 + O_2 \rightarrow 4 N_2 + 6 H_2O$), which is crucial for the formulation of high performance catalysts and for the development of numerical models, is still lacking. My PhD thesis is focused on the low temperature challenges of deNOx aftertreatment systems, and aims at elucidating the mechanistic aspects of the Standard SCR reaction and at developing industrially relevant and practical solutions for NOx emission control.

The first part of the work collects the most relevant results concerning the Standard SCR catalytic scheme. In particular, we analyzed crucial aspects of the reduction half cycle (RHC) and of the oxidation half cycle (OHC) in the redox mechanism of Standard SCR over Cu-CHA, which is nowadays one of the most eye-catching catalysts for the SCR technology. In the literature, while there is a general consensus that Standard SCR over Cu-zeolite catalysts proceeds via the reduction of Cu^{II} to Cu^{I} and the subsequent reoxidation of Cu^{I} to Cu^{II}, the detailed catalytic scheme is still debated. Firstly, dynamic kinetic data have been analyzed and simulated in order to gain insights into the reduction half cycle of Standard SCR. The results confirm that the RHC of Cu^{II} ions by $NO + NH_3$ is characterized by a 1:1:1:1 stoichiometry linking the amount of oxidized Cu sites, the consumption of NO and ammonia and the release of nitrogen. Specifically, this step involves the preferential consumption of Lewis ammonia, rather than the more stable Brønsted ammonia. Furthermore, the kinetic analysis of all our experiments are in line with a second order dependence of the RHC rate on the Cu^{II} fraction. This evidence seems hardly compatible with a single site mechanism, but rather suggests the participation of multinuclear Cu^{II} complexes. To study the oxidation half cycle of Standard SCR, a simple but effective protocol was proposed to probe the average Cu oxidation state of Cu-CHA, by measuring its extent of reduction in NH_3+NO flow. The data show that low temperature reoxidation of Cu-CHA by O_2 alone is possible, without intervention of additional gaseous or adsorbed species. By monitoring oxygen consumption in reoxidation experiments we have also demonstrated that this oxidation is extremely fast and that a NH_3 inhibition is possible for the reoxidation half cycle. Despite being very preliminary, the considerations here reported are important for the ongoing discussion of low temperature Standard SCR mechanism and hopefully will foster further discussion on how single Cu site reoxidation by O_2 can occur in the CHA framework.

The second part of my PhD thesis was developed in collaboration with Daimler A.G. and illustrates a novel technology designed to mitigate the cold start NOx emissions. The idea was born from our fundamental studies: the same chemical trapping mixtures, implemented to trap reactive NOx intermediates at low temperature, were also studied in view of practical applications for NOx emission control. Indeed, such systems (SCR catalyst + NOx storage material) featured an intrinsic dual functionality: they can operate both as NOx adsorbers, trapping NOx during the low temperature transient, and as SCR catalysts, reducing the previously stored NOx with NH_3 at higher temperatures. Accordingly, these mixtures have been renamed Adsorption + Selective Catalytic Reduction (AdSCR) systems. This concept prevents the need for an additional unit situated upstream of the SCR catalyst, being integrated into the existing aftertreatment systems by only modifying the washcoat formulation (**Figure 1**). The capability of chemical trapping mechanical mixtures (SCR catalyst + NOx storage material) to store NO in O_2 at low temperature has been analyzed also in view of practical exhaust gas aftertreatment applications (AdSCR system). The experimental data so far collected confirm that this system is able both to store NOx before ammonia dosage (i.e. below 170°C), and to reduce them with ammonia at higher temperature in the same device. Testing the AdSCR behavior under realistic conditions, we show that the negative impact of water and CO_2 on the AdSCR performance can be at least partially counterbalanced by increasing the amount of the SCR catalyst included in the AdSCR compositions, as well as by selecting NOx storage materials more resistant to CO_2 (e.g. CeO_2). Furthermore, the full storage time can be maximized by adopting a storage material with high NOx storage capacity (e.g. BaO/Al_2O_3 and CeO_2/Al_2O_3-based systems), and by incrementing the load of storage material.
When the catalyst is saturated by NH_3, the presence of BaO/Al_2O_3 in the AdSCR system allows not only to store NOx at low temperature, but also to improve the low temperature SCR activity, abating NOx with a higher efficiency than over conventional SCR catalysts. These promising results identify NOx Adsorber + Selective Catalytic Reduction catalyst systems as very interesting materials, which may pave the way to new catalyst formulations useful for overcoming the deNOx challenge associated with the engine cold start up transients.
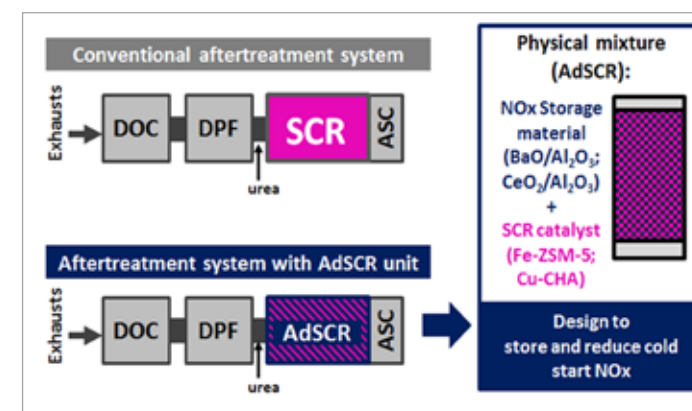

Fig. 1 - Comparison between a conventional aftertreatment systems and a modified aftertreatment systems with AdSCR uni

ADVANCED REACTOR AND CATALYST DESIGN FOR CONVENTIONAL AND SORPTION ENHANCED DIRECT DIMETHYL ETHER SYNTHESIS

Simone Guffanti - Supervisor: Gianpiero Groppi

Dimethyl ether (DME) is a promising alternative fuel with many possible applications: substitute for LPG, clean diesel for compression-ignition engines, hydrogen storage for fuel cells and fuel for power generations turbines. Moreover, DME is a valid product for the CO_2 utilization and the conversion of biomass to fuel. DME can be industrially produced by syngas (H_2, CO, CO_2) conversion via two routes: a two-step process consisting in the methanol synthesis followed by the methanol dehydration to DME (indirect synthesis), or a one-step process in which DME is obtained from the syngas coupling the two steps in a single reactor (direct synthesis). Differently from the indirect route, the DME direct synthesis is not a fully established industrial process and it is a subject of research focused on catalyst development, reactor and process design.

Different issues are associated to the direct DME synthesis, as first, the difficult thermal control: the direct synthesis of DME from syngas is indeed an exothermic process and a correct reactor design is fundamental for a proper heat management, in order to prevent excessive hot-spot temperature that leads to catalyst deactivation. The catalyst design is also challenging since different active phases, i.e. the methanol synthesis $Cu/ZnO/A_{l_2}O_3$ catalyst (CZA) and methanol dehydration to DME catalyst (γ-alumina or zeolites), need

to be coupled and this may result in a mutual deactivation due to the migration of some species (Cu, Zn and Si) between the two formulations. finally, the presence of high amounts of CO_2 in the syngas feed (as in the case of biomass gasification) coincide with a large production of water, that hinders both the kinetic and the thermodynamic of the process. The aim of this thesis is the development of mathematical models of chemical reactors for the simulation and design of industrial scale equipment for the direct synthesis of DME from biomass gasification syngas, containing variable and larger content of CO_2 if compared to traditional feedstock (e.g. syngas from natural gas). The models provide an accurate description of all the significative chemical and physical phenomena occurring inside of the reactors, with particular focus on the

thermal behavior, which plays a key role in a correct reactor design. The work includes both the modelling analysis of conventional multitubular externally cooled fixed bed reactors and of advanced reactors exploiting the concept of sorption enhancement. Sorption Enhanced DME Synthesis (SEDMES) is a promising process solution for the issues related to water production with CO_2 rich syngas. SEDMES consists in the coupling of direct DME synthesis catalysts with selective in-situ water adsorbent materials (such as LTA zeolites) (Fig. 1), in order to shift the thermodynamic equilibrium limitations with a consequent improvement of reactant conversion and DME yield independently from the CO/CO_2 ratio in the feed.
The thesis work starts with a thermodynamic analysis of SEDMES, in which are explored
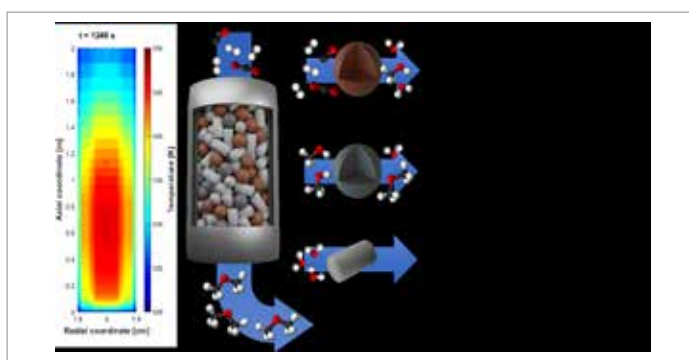

Fig. 1 - SEDMES reactor tube temperature profile at fixed time and schematic representation of SEDMES process.

the performances of the process in different operating conditions (considering temperature, pressure and inlet composition). The analysis includes also the investigation of the 'SEDMES reactor train', a process configuration in which a SEDMES unit is coupled with a conventional converter and a water separation unit, positioned upstream, in order to reduce its heat and water duties. The next part consists of the analysis and design of the conventional direct DME synthesis reactor operating in a wide range of conditions, accounting in particular for different CO/CO_2 inlet ratio. The results show that in order to control the temperature relatively small tube diameters (25.6 mm) must be used. A dedicated section is focused on the effects of the active phase distribution at the catalyst pellet scale on the reactor performances. Different active phase distributions of CZA and acid catalyst (hybrid pellets, mechanical mixture of methanol and dehydration catalyst pellets, core@shell engineered pellets) (Fig. 2) are analyzed, interpreting the results through the
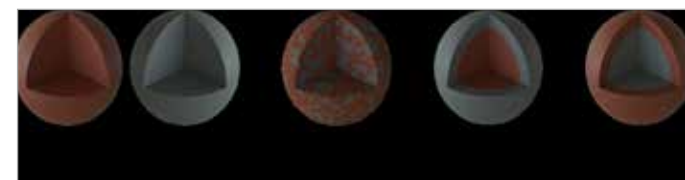
analysis of the reaction-diffusion phenomena inside the catalyst pellets, highlighting the importance of the intraparticle diffusion limitations on the consecutive reaction scheme involved in the direct DME synthesis process. MeOH@DME core@shell pellets are identified as a promising solution, which combines high catalyst efficiency and selectivity to DME with relatively mild temperature profiles, while minimising the contact between the two formulation thus decreasing deactivation risks.
The last section is related to the development of a dynamic model used for the analysis and design of the SEDMES reactor unit. The model, validated by comparison with experimental bench scale data, describes the dynamic profiles of composition and temperature inside the reactor during the reaction/ adsorption step, allowing for a rational design of the unit. It is confirmed that, thanks to the beneficial effect of in-situ water removal, with SEDMES is possible to obtain high DME yield independently from the CO/CO_2 ratio. Moreover, the dilution of the catalyst

in the adsorbent material allows to operate with larger tube diameters (up to 46.6 mm) with respect to conventional direct DME synthesis, despite the higher exothermicity of SEDMES process due to the additional heat released by water adsorption.

Fig. 2 - Catalyst pellet configurations sketch. Brown – CZA (MeOH) catalyst; grey – γ-Al_2O_3 (DME) catalyst.

A STUDY ON POLYMER PRODUCTION SYSTEMS: PROCESS UNDERSTANDING, SWITCH TO CONTINUOUS AND NOVEL APPLICATIONS

Juri Ilare - Supervisor: Davide Moscatelli

Co-supervisor: Mattia Sponchioni

he care of safety and environment is nowadays an essential aspect in the conduction of every kind of production process. In the specific case of free-radical polymerization (FRP), discontinuous processes suffer from many limitations with respect to safety, productivity, product quality and cost. In this sense, during the last years important efforts have been done in the attempt to convert the traditional batch polymer production to continuous processes. This, in turn, facilitates the fulfilling of the more and more stringent requirements imposed by local and international regulatory agencies with respect to safety conduction and hazardous emissions. In addition, through this process intensification, it is also possible to optimize both investment and operative costs, thus overcoming the current profit margin reduction in the field of polymerizations.

Chapter 1 provides an insight into the technical and process difficulties that are currently hampering the transition from batch to continuous FRPs. The discussion is driven by considering key points in polymer manufacturing, including safety, environmental concerns, product quality and cost management. For a seek of clarity, we drove the discussion by considering the two main modalities in which the FRP can be conducted, namely homogenous and heterogeneous reactions. Extensive reference

to literature examples is made to highlight the state of art in the field and the recent innovations towards continuous processes. Finally, successful examples of such auspicable transition achieved on an industrial scale are presented, trying to highlight the features that can be generalized to reach the goal. Afterwards, we propose two case studies that discuss this worthwhile transition considering two of the most appealing monomers for the market, namely acrylic acid (AA) and methacrylic acid (MAA).

Specifically, Chapter 2 reports a model-assisted strategy for transferring the solution FRP of nonionized AA from batch to continuous with the aim of preserving the product quality, in terms of weight-average molecular weight. A basic kinetic model is developed and validated by comparison with experimental results for three reactor configurations, batch, semibatch and continuous stirred tank reactor (CSTR). Then, examples of transferring a semibatch recipe to continuous, using a stirred tank reactor, are analysed. Taking advantage of the validated model, a successful transition is designed through an optimization procedure. Based on a minimum acceptable monomer conversion of 98%, an increase in the polymer productivity up to 88% is achieved. Towards the same aim of process

intensification, Chapter 3 reports a model-based strategy to convert the solution free-radical polymerization of non-ionized methacrylic acid from semibatch to continuous while preserving the product quality in terms of average molecular weight and polymer content. First, the kinetic scheme and the corresponding set of mass and population balance equations are validated in three different reactor configurations, batch, semibatch and continuous stirred tank reactor. Then, a basic optimization approach is applied to guide the transition of a selected semibatch process to a continuous one conducted in a CSTR. This strategy results in a substantial productivity increase (productivity ratio between CSTR and semibatch equal to 5.1) while preserving the selected polymer average molecular weight and dry content. Finally, in order to reduce the residual monomer in the product leaving the CSTR, we simulated the addition of a tubular reactor. This was modelled introducing a small plug flow reactor (PFR) in series to the CSTR. This approach represents an effective and robust tool for polymer manufacturers to assist switching their productions to continuous with minimal experimental effort while preserving their product portfolio.

After this thorough investigation on polymer production processes and intensification, this research

is addressed to the improved utilization of engineered polymer nanovectors in the field of cosmetic and detergency. In fact, the market of cosmetic and personal care products is continuously growing its impact. In particular, the products that are currently driving this growth have a strict connection with fragrances (e.g. perfumes, detergents, body creams, and softeners). In this framework, synthetic polymers are attracting growing attention as additives for laundry and personal care products. In particular, the high volatility of many common fragrances requires the development of polymeric particles for their encapsulation and controlled release. Unfortunately, the vast majority of these carriers are made from polymers that are not biodegradable. This poses severe concerns about the accumulation of nano- and microplastics. Hence, such particles are expected to be banned from the market in the coming years. Therefore, biodegradable particles enabling a long-lasting release of the fragrances are urgently needed.

In Chapter 4, we study the production of biodegradable nanoparticles (NPs) that are structurally composed of lactones, i.e. well known perfumes that occur naturally and that are already considered safe by regulatory agencies. We polymerize these lactones via ring opening polymerization (ROP)

using an ionizable tertiary amine as initiator to produce in a single step amphiphilic oligoesters able to directly self-assemble into NPs once nanoprecipitated in water. In this way, we can produce biodegradable NPs with a perfume loading up to 85% w/w without the need for additional surfactants. Subsequently we show that the ionizable group is able to confer a positive charge to our nanoparticles and, in turn, a high adsorption capacity on natural fibers (i.e. hairs and cotton fabric). Finally, we demonstrate the nanoparticle resistance to rinsing and their ability to confer a long-lasting fragrance perception to treated hair swatches for at least 3 weeks. In any case, traditional acrylic NPs are still playing a pivotal role for delivering fragrances characterized by a typically high volatility. More in detail, it is highly desirable to maximize the interaction between the carrier and the substrate, which would avoid the NP desorption following scrubbing and repeated washing. In the case of laundry products, limited NP desorption is also crucial to prevent the accumulation of nanoplastics in the environment, which is nowadays strictly regulated. Therefore, a thorough study highlighting the influence of the different physicochemical properties of the NPs on their adsorption behavior is urgently required.

In Chapter 5, we propose a study on

the synthesis of polymer NPs with different size, surface charge, glass transition temperature, and degree of cross-linking through emulsion free-radical polymerization to investigate how these parameters affect the NP adsorption onto a textile substrate (composition: 90% cotton/10% elastane). This study can provide interesting guidelines in the design of new fragrance delivery systems as well as in the optimization of those already adopted in the market. Finally, we investigate the possibility of loading and mediating the release in air of limonene, one of the most common odorous molecules in the cosmetic field, overcoming its well-known volatility.

ODOUR EMISSION ESTIMATION FROM COMPLEX SOURCES AND DISPERSION MODELLING

Marzio Invernizzi - Supervisor: Selena Sironi

The research field related to the study of odour nuisance resulting from gaseous emissions from industrial settlements is in great expansion. This is mainly because the scientific community has paid little attention to these problems: the sense of smell has often been considered a sense, "ridiculous", to laugh at, not to be studied.

Three specificities make the odour impact assessment different from the classic analyses on classic macro-pollutants.

The first is that chemical analysis is a little effective tool in this case: the smell, in fact, is a psychometric stimulus that resides in the nervous system of the person who smells. Therefore, the chemical analysis cannot provide direct information about the odour potential of a gaseous mixture. Only in case of single odorant gases (in air) the Odour Threshold Value (OTV) can provide, the odour concentration. Unluckily, it is rare that a single chemical compound causes the environmental odour: the odour is often perceived due to the presence of a huge amount of different chemicals in mixture. In these cases, the single OTVs cannot provide reliable results: the interaction phenomena among different molecules are far from being well understood.

The solution is to treat the nose as a "black box" and use a group of people, duly selected. This technique is called dynamic olfactometry, and is able to measure the concentration of smell, expressed in ou_E/m^3: this value indicates the number of neutral air dilutions necessary for the sample to be no longer perceived by the panel of selected people.

The second peculiarity of odour impact assessments is that often, emissions do not come from a few large channelled sources, such as stacks: in those cases, it would be relatively easy to measure flow rate, physical parameters and concentration. Odorous emissions often come from sources that we could define as complex: they are all those sources that can potentially cause a release of odorous emissions but whose quantification is not trivial. Example of complex sources are diffuse emission from a wastewater treatment basins or storage tanks.

The third aspect that differentiates olfactory impact assessments from those of macro-pollutants is that the impact is quantifiable as "How much the receptor perceives", not "What does the plant emit". For this reason, the overall majority of the odour impact assessments are carried out through the use of atmospheric dispersion models. Despite the Odour Emission Rate (OER) is a key input parameter for these models, to assess if and how much the emission reaches the receptor location, different other parameters play an important role: meteorological conditions, geometric and physical features of the sources and the chorography of the area.

The vast majority of current dispersion models have been designed to predict pollutant concentrations on an hourly basis, overlooking information on sub-hourly short-duration events. Due to the importance of concentration fluctuations in odour exposure, there has recently been an increasing interest in modelling techniques
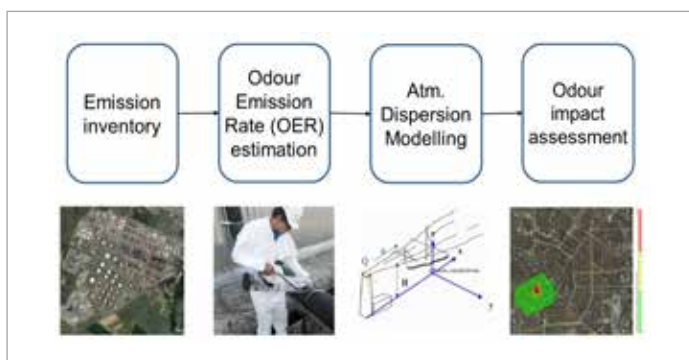

Fig. 1 - Odour Impact Assessment: steps needed for the execution

capable of providing information on these kinds of sub-hourly episodes. Aware of the vastness of the topics that would need to be explored, my PhD project aimed to improve the state of the art of different technical aspects, necessary for odour impact assessments. To give a brief overview, the steps needed for an odour impact assessment are reported in Figure 1.

My research work focused on the investigation two critical aspects in the state of the art of odour impact assessment: the characterisation of complex sources and the assessment of ambient concentration peak phenomena.

Firstly, emission from liquid area sources has been investigated. In particular two theoretical and experimental analysis were conducted, in order to describe the emission behaviour of different complex sources. At the beginning of PhD period an analysis on quiescent liquid basins, based on Wind Tunnel measurements, has been conducted. A further research has investigated the aerated liquid surfaces, like active sludge oxidation basins.

In parallel, another kind of complex odour source are investigated: hydrocarbon storage tanks. The emission of Volatile Organic Compounds VOC, which can cause odour emissions, from these facilities is analysed, and the state of the art of

the emission quantitative estimation has been critically reviewed. Some possible improvements of the available methods have been developed in software codes. Unluckily, mass flux are not enough to characterize the odour flux: a new experimental method, to link the mass flux and the OER, is presented. By this it is possible to assess the Hydrocarbon Odour Emission Capacity (HCOEC) of an oil cut: it represents how many odour units (ou_E) are released by the evaporation of a known amount of hydrocarbon mixture (kg). Essentially we developed the method to measure "How much gasoline smells?". A scheme of the experimental apparatus is depicted in Figure 2.

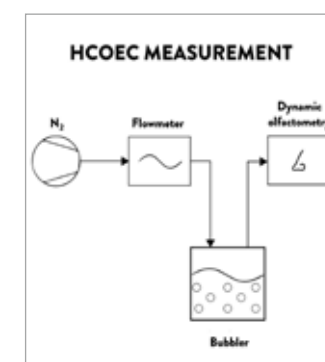In order to test the reliability of the method, different repeated trials and MonteCarlo simulations have been

Fig. 2 - HCOEC experimental equipments

conducted, showing repeatability results with at least 1 digit of significance.

As a last part of this PhD research the output of odour dispersion modelling has been analysed: how the short-term concentration fluctuation can be modelled?

First of all, an analysis and a comparison of different available dispersion modelling software (CALPUFF, LAPMOD and GRAL) was conducted. After that, a new analytical Fluctuating Plume Model has been developed, in order to assess, with a simple Gaussian model, data about the short-term ambient concentration. Actually, it provides the calculation of concentration variance at receptors: in this way, by stochastic considerations, it is possible to estimate the short-term odour peaks.

CO$_2$ HYDROGENATION TO SYNTHETIC NATURAL GAS: EXPLOITING THE POTENTIAL OF RU–BASED CATALYSTS

Alessandro Porta - Supervisor: Luca Lietti

In order to reduce the CO$_2$ emissions and comply with international agreements, a strong increase in the use of renewable energy and carbon capture technologies is foreseen. Renewables are intrinsically fluctuating sources, and this leads to periods of power overproduction which needs to be effectively stored. A valid solution is provided by the Power to Gas (PtG) technology. This process uses the excess power to split water and produce H$_2$ (and valuable O$_2$), which is then reacted with CO$_2$ to form CH$_4$ and H$_2$O through the Sabatier reaction. Among all the possible products of CO$_2$ hydrogenation, methane has the huge advantage to have an already-existing infrastructure for its transport and use. The methanation process is generally carried out over Ni-based catalysts, but from a process intensification standpoint, also the less investigated Ru-based catalysts are of interest. Indeed, it is known that Ru is the more active metal for the Sabatier reaction, and hence allows the feasibility of such reaction at lower temperatures with respect to Ni-based catalysts, allowing to achieve higher per-pass CO$_2$ conversions and to operate at low pressures. In this context, the first part of this thesis aims at the optimization of the efficiency of the CO$_2$ methanation process at industrially relevant conditions on Ru/Al^{2}O$_3$ catalysts (Figure 1).
Initially, the effect of the metal loading

and of the size of the catalytic support has been investigated, revealing insights on the optimal Ru loading and on the onset of transport limitations. These findings provide guidance on how to exploit at best the costly active phase.
When using low Ru loading (0.5 wt.%), it has been found that eggshell catalysts are obtained via impregnation on large Al$_2$O$_3$ pellets due to the interaction between the Ru precursor and the support (Fig. 1a). However, this interaction can be modified in order to effectively tune the thickness of the catalytic layer. Nevertheless, at such low metal loading, when varying the dimension of homogeneously impregnated pellets, no significant differences in the catalyst activity were observed, indicating the absence of diffusional limitations even on large pellets. Aiming at increasing the catalyst activity, the effect of Ru loading has been also investigated in the range 0.5 – 5 wt% under kinetically

controlled conditions. The adopted preparation method allowed to obtain highly dispersed systems, with Ru average particle diameters below 2.5 nm (Fig. 1b). No relevant differences in CO$_2$ conversion nor CH$_4$ selectivity have been observed while working at constant flowrate per gram of Ru, despite the decrease in Ru surface area with increasing metal loading. This implies that, in the investigated particle size range, the loss in catalytically active surface is effectively counterbalanced by the increased intrinsic reactivity (turnover frequency) of the remaining Ru sites. This has been explained through the structure sensitivity of the Sabatier reaction on Ru-catalysts.
In order to investigate the effect of the catalyst support size, the recipe showing the highest turnover rate per gram of catalyst (5 wt% Ru/Al$_2$O$_3$) has been replicated using supports of 800 and 2300 μm. In these cases, the conversion and selectivity of the process diverge from the result

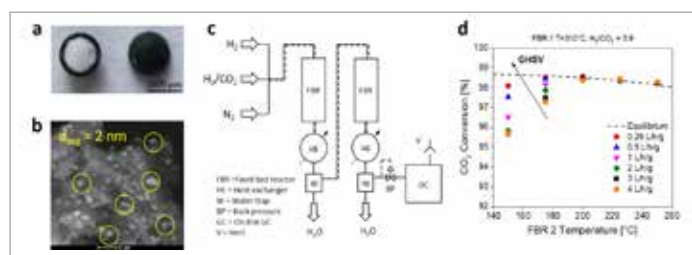obtained in a kinetically controlled regime. As a result, lower methane yields are obtained with increasing catalyst particle size because of the slow diffusion of CO$_2$ within the catalyst pore system and the slow heat removal at the gas solid interface. This makes highly active Ru-based materials more attractive for compact packed reactors, where pressure drops are less relevant and smaller pellets can be used, or washcoated systems.

The feasibility of a CO$_2$ methanation process able to reach CO$_2$ conversion levels in excess of 98% with a complete CH$_4$ selectivity has been also demonstrated exploiting Ru/Al$_2$O$_3$ catalysts. Using a simple process configuration (Fig 1c) and operating at atmospheric pressure, it is possible to produce a gas stream able to meet, without further purifications other than water removal, the stringent purity thresholds required for the direct injection of the produced synthetic natural gas (SNG) into the gas grid (Fig 1d). Furthermore, the stability of the Ru/Al$_2$O$_3$ catalyst has been investigated for nearly 600 h in presence of concentrated H$_2$/CO$_2$ streams and almost complete conversion levels and no relevant deactivation phenomena have been observed.
The second part of this thesis is dedicated to the study of doped Ru-based catalysts for the CO$_2$ capture and methanation process. In most applications, CO$_2$ comes from conventional carbon capture technologies, which are energy intensive. A possible solution to the high energy demand is represented by the combined capture and hydrogenation of CO$_2$. The idea is to capture CO$_2$ from a CO$_2$-containing

stream (e.g. combustion flue gases) with a catalytic material that acts as a solid adsorbent, and then exposing the CO$_2$-saturated material to a renewable H$_2$-containing stream in order to produce CH$_4$ and regenerate the adsorbent. The typical catalyst formulation consists of an alkaline or alkaline-earth metal as adsorbing agent and Ru as methanation catalyst, both supported on a high surface area carrier.
In this context, mechanistic aspects involved in the CO$_2$ storage and reduction to methane have been analyzed by using a model Ru-Ba bifunctional catalyst. In particular, the role of the Ru-Ba interaction in the reaction has been deepened, by comparing the catalytic behavior of a bimetallic Ru-Ba/Al$_2$O$_3$ catalyst and of a Ba/Al$_2$O$_3$ + Ru/Al$_2$O$_3$ mechanical mixture. It has been found that the presence of Ru does not affect the CO$_2$ storage capacity. At variance, the reactivity of the stored CO$_2$ is strongly affected by the presence of Ru, and when both storage and hydrogenation components are present on the same support, the reaction occurs at much lower temperatures. Furthermore, the effects of different representative CO$_2$ adsorption con conditions (H$_2$O, O$_2$, NO$_x$) during the capture phase have been investigated.
The stability of these catalytic materials is probed by means of aging cycles at simulated flue gas conditions. It has been found that these materials demonstrate a steady, yet very subtle, loss in the amount of CH$_4$ produced per cycle. The observed deactivation depends on the Ru loading and has been ascribed to an irreversible sintering of Ru particles upon O$_2$ exposure at high temperature.

Fig. 1 - a) 2.3 mm 0.5% Ru/Al2O3 eggshell catalyst section; b) HR-TEM results on a 5% Ru/Al$_2$O$_3$ catalyst; c) sketch of the optimized layout of the experimental rig; d) experimental CO$_2$ conversion.

BIOGAS TO LIQUID (BIGSQUID™) FROM FEASIBILITY STUDY TO PILOT SCALE

Daniele Previtali - Supervisor: Flavio Manenti

Humankind is facing an unprecedented challenge; global warming is a recognized fact and its consequences, insignificant for the planet Earth, could be devastating for living beings. Carbon dioxide (CO_2) is the main responsible for global warming and we should reduce its quantity in the atmosphere by 1000 Gt compared to 2011. In 2018, we emitted 33.1 Gt of CO_2 and the energy sector is the main responsible causing about 75% of all the greenhouse emissions. The increase of renewable energy share (solar, wind, geothermal...) will have a key role to lower our carbon footprint but IEA estimates that to reach a sustainable development scenario the use of renewable energies as substitution of fossil fuels will not be enough and additional policies are necessary. The use of greener fossil fuels and the increase of nuclear energy production are other important approaches to the medium term. The most interesting short-term strategy is Carbon Capture Utilization and Storage (CCUS). CO_2 storage consists of its underground injection and absorption or mineralization over solids or liquid. This technology can be very effective to reduce CO_2 emissions of fossil fuels but its costs are very high, and today are the limit. Direct use of CO_2 is an alternative process to CCS and should be preferred, chemical conversion and re-use of CO_2, by a technological point of view, is smarter

than simple storage or landfill and can be inserted in complex economy logics. Decarbonization of the energy sector potentially is relatively simple, decarbonization of the chemical industry is not. Chemistry is based on carbon molecules and the use of CCU is the only method to avoid extraction of further carbon from the soil in the form of oil, coal or natural gas. The cost of CO_2 capture is strictly correlated with CO_2 content in the stream, for this reason biogas is one of the most interesting streams.

Biogas is produced by anaerobic digestion of organic matter and is mainly composed by methane and carbon dioxide. Today biogas is used as energy source inside Combined Heat and Power (CHP)

plants or upgraded to biomethane, via removal of carbon dioxide, which is injected in the national natural gas distribution grid. Both the processes are not economically sustainable, and the profitability is reached thanks to governmental incentives. The environmental impact of biomethane and CHP plants is considered negligible because the organic matter come from fixed atmospheric CO_2, even though real emissions are not zero since all the processing steps should be considered. Thus, it is important to evaluate alternative uses of biogas, associated with lower carbon emissions like the novel concept of Combined Heat, Power and Chemical (CHPC) plant based on BigSquid™ technology. In a CHPC plant, as small portion of biogas is still
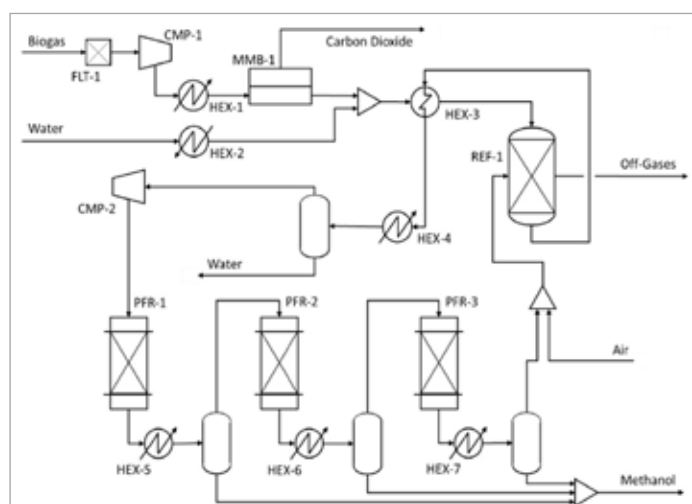

Fig. 1

converted into heat and power, but the largest amount is converted into chemicals such that carbon atoms are partially fixed instead of being released back into the atmosphere as CO_2. This is only a temporary storage, carbon soon or later is re-emitted as CO_2, but allows to reduce the use of fossil sources, such as methane and oil. Methanol has been chosen because widely utilized as solvent, fuel and building block for the synthesis of formaldehyde, dimethyl ether acetic acid and synthetic fuels. The CHPC plant (Fig.1) is divided in two main unit operations, a reformer and a methanol reactor; the first one converts biogas into syngas while the second transforms syngas into methanol. A bench-scale plant has been built to study the effects of alkaline earths as promoters toward syngas conversion into methanol at low pressure. The optimal configuration of CHPC has been studied using PRO/II, a well-established process simulation suite by AVEVA (former Schneider-Electric). The optimization of the operating conditions has been done using PRO/II built-in optimizer and an external robust optimizers called CORO software. Guthrie's method algorithms estimated investment and operating costs. The environmental impact of CHPC has been assessed using SimaPro software and compared with alternative processes such as CHP and biomethane upgrading

plants. Finally, the BIGSQRT, a C++ based software, modelled the entire CHPC process. BIGSQRT allowed to simultaneously optimize the environmental impact and economic cost of the CHPC process using multi-objective optimization. Moreover, using optimization with uncertainty algorithms, robust optimal operating conditions have been calculated to increase the flexibility of this novel process. The principal source of uncertainty considered was variations in the biogas feedstock composition, an extremely important aspect due to the intrinsic instability of biogas composition as function of biomass feedstock and time. Results show that CHPC process is technically and economically feasible. CORO and BIGSQRT are two important and useful tools for process optimization, the first is more generic and compatible with several process configurations while the second is specific for the CHPC process and so it has better performances than CORO. CaO results to be the most interesting CZA promoter and in some condition has better performance than the commercial catalyst, using syngas the methanol productivity can increase up to 2.5 times. CZA promoted with strontium resulted inactive (conversion lower than 5%). The environmental analysis confirmed that the carbon footprint of CHPC is lower than CHP and biogas upgrading plant. Otherwise, the presence of catalysts

and the larger water consumption result in higher human toxicity and water depletion for CHPC. A CHPC plant with a feed of 500 Nm³/h of biogas can produce up to 397 kg/h of methanol with a payback time of about 8 years without governmental incentives.

AN INTERFACE-RESOLVED METHODOLOGY FOR THE EVAPORATION AND COMBUSTION MODELING OF ISOLATED FUEL DROPLETS

Abd Essamade Saufi - Supervisor: Alberto Cuoci

Multiphase flows are extensively used for power generation (e.g. internal combustion engines, gas turbines, industrial burners), due to the high energy density of liquid fuels. The combustion of a liquid is generally carried out through an atomization process, transforming the liquid in a spray of droplets, followed by the fuel vaporization, ignition and gas-phase combustion. The improvement and control of a spray system is not only beneficial from an economical point of view, but it significantly impacts its efficiency in terms of pollutants emission. The collective vaporization of the droplets ensemble directly influences the burning rate and the combustion chamber performance. The simplest and physically meaningful configuration we can extract from a spray system is represented by an isolated droplet: this allows to put aside the physical interaction phenomena typically involved in gas-liquid dispersed flows (breakups, coalescence, fragmentation etc.), obtaining an ideal system for the analysis of vaporization, ignition and combustion of liquid fuels. Isolated droplets are mainly studied assuming a spherical symmetry of the system in order to simplify the mathematical modeling and leave room for a more detailed chemistry description: this approach paved the way for the study of crucial aspects related to microgravity combustion, such as cool flames,

multiple ignitions and extinction regimes.

The main drawback is that external convection, internal circulation, interface deformations and other essential phenomena cannot be described, despite their fundamental role in droplet vaporization. This work aims at addressing these issues, proposing and discussing a numerical model for the combustion of isolated droplets based on an interface-resolved approach, i.e. including momentum equations for the velocity field and the advection of the fluid interface, abandoning the sphero-symmetric hypothesis. The main novelty is the extension of the two-phase fluid dynamic core to include (i) heat and mass transfer rates based on the resolution of the boundary layer (without the use of semi-empirical correlations), (ii) a detailed treatment of thermodynamics at the interface, (iii) multicomponent fuels, (iv) the phase-change process, (v) the gas-phase combustion and (vi) the thermal

interaction with the suspending fiber. In addition, one of the main critical problems in the CFD modeling of evaporating droplets is the numerical treatment of surface tension, due to the persistent presence of an artificial velocity field (spurious currents) which destabilizes the interface. In this work this problem has been approached introducing (vii) a suspending force, directed towards the droplet center, which stabilizes the droplet against gravity and eliminates the spurious currents instabilities. The resulting code is called DropletSMOKE++ and it shows a very good agreement with the experiments in a wide range of operating conditions, both in natural and forced convection.

The comparison with the microgravity condition highlights the impact of the external fluid flow on the evaporation mechanism, while non-ideal thermodynamics is shown to be fundamental to model high pressure systems and multicomponent droplets. The analysis of droplet
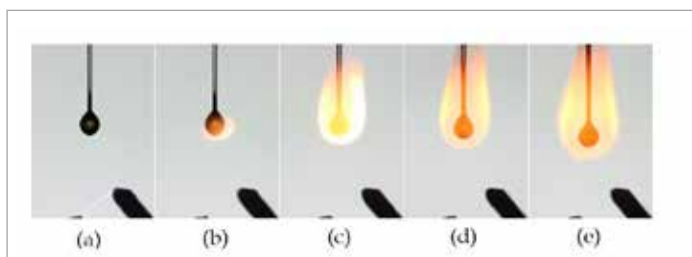
combustion is reported in terms of standoff ratio, flame temperature, internal circulation and water condensation, exhibiting a satisfactory agreement with experiments in terms of diameter decay, temperature profiles and sensitivity to the gas-phase oxygen concentration. In particular, the multiregion approach is shown to be essential to describe the conjugate heat transfer between the solid fiber and the fluid phase, which enhances the burning rate and causes a partial quenching of the flame close to the wall. Finally, the problem of spurious currents has been approached in a more rigorous way: DropletSMOKE++ is extended to include a stable and accurate methodology for surface tension, based on a combination of the Ghost Fluid Method (GFM) and Height

Functions (HF). The method is able to reduce spurious currents almost to machine accuracy and accurate results are obtained for additional cases such as translating droplets, capillary oscillations, rising bubbles, sessile droplets and suspended droplets.
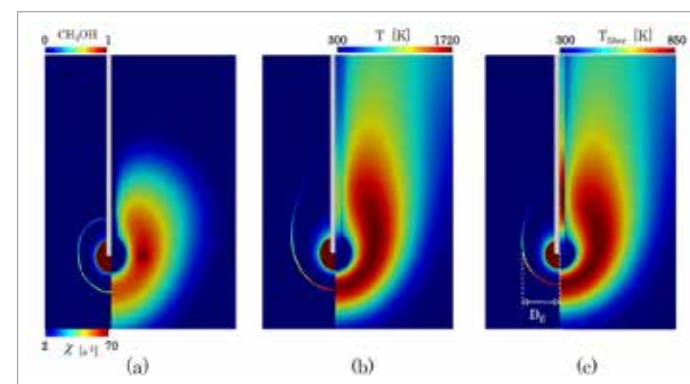

Fig. 1 - Fuel droplet combustion experiment in normal gravity conditions

Fig. 2 - Case 2: 2D maps of methanol mass fraction (left), fluid and solid temperatures (right) at times t = 0.07 s (a), t = 0.5 s (b) and t = 1 s (c). On the left side the stochiometric passive scalar contour is shown, colored by the scalar dissipation rate. The flame diameter definition is evidenced in (c).

PHYSIOLOGICALLY-BASED APPROACH TO PHARMACOKINETIC MODELING FOR CLOSED-LOOP CONTROL OF ANESTHESIA AND OPTIMIZATION OF DRUG DOSING IN INTENSIVE CARE

Adriana Savoca - Supervisor: Davide Manca

Despite recent technological advances in biomedicine, the availability of model-based tools to support medical doctors in clinical decision-making is rather limited. The selection of the optimal drug dose and dosing regimen is a complex problem, which must take into account the physical characteristics of the patient and is constrained by patients' co-morbidities and therapeutic windows of drugs. This work focuses on the specific fields of anesthesia and intensive care. Anesthesia-associated risks are mostly related to medication errors, typically associated to the administration stage. In the intensive care unit (ICU), wrong dosing is reported as one of the most frequent errors. Anesthesia and intensive care share significant challenges, such as nonlinear and complex dynamics of the patients' response to drugs, uncertainty of the dose-response relation (because of high inter- and intra-individual variability), multiplicity of variables characterizing and describing the response, and operative constraints (therapeutic windows of drugs and safe clinical ranges of patients' physiological parameters). Clinical adoption of model-based tools for selection of the optimal dose can bring actual improvements in these fields, by providing a more rigorous and robust approach to inter-individual variability of the response to drugs, reducing clinicians' workload

and variability in practice, and limiting potential human errors. Combination of medical doctors' experience and knowledge with such tools can guide the decision-making process and enhance patients' safety and quality of recovery.

This work can be divided into two parts. The goal of the first part is to develop and evaluate in silico a physiologically-based (PB) model-predictive controller for closed-loop administration of the anesthetic agent propofol and the analgesic opioid remifentanil. In clinical practice, anesthesiologists select an initial dose to induce the desired depth of anesthesia and then make adjustments basing on the monitored physiological parameters, to maintain the desired depth of anesthesia throughout the medical procedure that requires the anesthetic state (e.g., surgery). For the sake of completeness, it is worth mentioning that in many parts of the world, Target-Controlled Infusion (TCI) pumps (a model-based technology) are commonly used to deliver intravenous anesthesia. However, their performance is totally dependent on the accuracy of the embedded model and does not take into account patients' real-time data on physiological parameters. Anesthesiologists heavily rely on their experience and knowledge, setting the basis for remarkable variability of the procedure and

potential human errors (related to the level of attention, stress and fatigue, and quality of communication with the rest of the operating room team). Researchers are investigating closed-loop solutions for automated anesthesia delivery. Proposed solutions differ for selected control strategy (e.g., model-free or model-based), number of inputs (considered physiological parameters), and number of outputs (considered drugs). In our work, we consider both a quantitative measure of hypnotic depth and hemodynamic parameters to regulate propofol and remifentanil infusion rates, for a complete control over the anesthetic state of patients. In addition, the use of the modern physiologically-based approach to pharmacokinetic-pharmacodynamic modeling allows facing some of the most controversial challenges of anesthesia delivery, i.e. (i) optimal dosing in "at-risk" categories of patients (in particular, elderly, obese, and pediatric patients) and (ii) investigation and inclusion of the impact of hemodynamic changes on the patients' response and required dosing modifications, which are crucial for a smooth procedure and post-operative recovery. Special attention is also devoted to propofol-remifentanil synergistic effects on arterial pressure.

The goal of the second part of the work is to develop a multi-route PB pharmacokinetic model of melatonin

for administration to critically ill patients, with the purpose of optimizing melatonin delivery for this special category. Indeed, melatonin is a well-known sleep regulator and is currently of great interest for its additional functions, e.g., anti-oxidant, immunomodulatory, and anti-carcinogenic effects. Sleep disruption is a common problem in ICU and has short- and long-term adverse effects on the patients, with the risk of further compromising their recovery. Melatonin versatility to multiple routes of administration and lack of toxic effects makes it extremely appealing for application to ICU. Researchers are investigating its pharmacokinetics in both experimental and simulation studies. This work moves a step forward by showing how the proposed PBPK model can be applied to identify (i) the optimal administration route depending on the goal of the clinical treatment and (ii) the most suitable dose, dosing regimen, and time of administration according to the selected route. Although the work focuses on melatonin, the proposed approach is valid for any drug for which an ideal pharmacokinetic profile is desirable.