25
JUNE
2013

SYMPOSIUM
‘FRONTIERS IN CHEMICAL REACTION ENGINEERING’

Technology Park 904, Zwijnaarde

UNIVERSITEIT
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FACULTY OF **ENGINEERING AND ARCHITECTURE**

CONTENT

Contributions

erc European Research Council

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SYMPOSIUM (BUILDING 904)
‘FRONTIERS IN CHEMICAL REACTION ENGINEERING’

8.30 am Welcome with coffee and registration

9 am Opening by Guy Marin

Contributions:

- ‘Understanding and Predicting Complex Gas Phase Kinetics’ by William Green, MIT, Cambridge USA
- ‘Bifurcation analysis of an industrial process’ by David West, SABIC Technology Center, Sugar Land USA
- ‘Modelling heterogeneous catalysis at a molecular scale: insights from DFT’ by Philippe Sautet, Université de Lyon and CNRS

11.50 am Lunch and registration

1 pm **Contributions:**

- ‘Deacon chemistry revisited: new catalytic processes for chlorine recycling’ by Javier-Perez Ramirez, ETH, Zürich, Switzerland
- ‘CFD modeling of flow, mixing and reaction’ by Rodney Fox, Iowa State University, USA
- ‘Multiscale Simulation of Chemical Reactions and Reactors: Combinatorial Complexity, Uncertainty, and Emergent Behavior’ by Dionisios Vlachos, Delaware University, Wilmington USA
- ‘Coiled flow inverter - Novel Device for Process Intensification’ by Krishna Nigam IIT, New Delhi India

4 pm Conclusion and visit of Technical Hall 918

5 PM – INAUGURATION CEREMONY BUILDING 914

5.30 pm Visit of Technical Chemistry wing and reception

UNDERSTANDING AND PREDICTING COMPLEX GAS PHASE KINETICS

by W.H. Green, Hoyt C. Hottel Professor & Executive Officer,
MIT Dept. of Chemical Engineering

A long term goal of the chemical R&D community is to move from being an empirical field, where advances are largely via Edisonian trial and error experimentation, to being a predictive science, where the innovation cycle could be accelerated by computer-aided design. Research at LCT and collaborating institutions has brought this goal within reach for gas-phase pyrolysis chemistry of small organics. However, the complexity of the chemistry remains a major challenge, particularly as we try to understand larger molecules and a broader range of chemistries. The current status of this effort will be reviewed, and some directions for the future outlined.

BIFURCATION ANALYSIS OF AN INDUSTRIAL PROCESS

by David West, Corporate Fellow, SABIC, Sugar Land, Texas, USA

Jet-stirred reactors are commonly used in industry for highly exothermic reactions such as chlorination, hydrodealkylation, nitration, and combustion. Reactants are injected into a larger diameter pipe in a sudden expansion type flow. The high velocity feed jet drives recirculation to achieve mixing between reactants and products. For sufficiently exothermic reactions, multiple steady state conditions are possible. In the ignited state, conversion remains essentially constant over a wide range of flow rates until an extinction point is reached, beyond which the reaction rate drops dramatically. Operation near the extinction point is very sensitive to small fluctuations in control variables. Analysis of pressure data in normal operation reveals small scale chaotic oscillations. The amplitude of these oscillations grows in the neighborhood of the extinction point, a property that can be used for early warning of incipient extinction. External perturbations of the right frequency are amplified within the reaction zone causing sudden, intermittent, large amplitude pressure spikes, causing reactor control problems. The dynamics appears to arise from a Shilnikov (homoclinic saddle-focus) bifurcation. A deeper understanding of these phenomena will be presented along with strategies to better stabilize reactor operation.

MODELLING HETEROGENEOUS CATALYSIS AT A MOLECULAR SCALE: INSIGHTS FROM DFT

by Philippe Sautet, Université de Lyon, CNRS, Institute of Chemistry, Lyon, France

Heterogeneous catalysis is today at the core of sustainable chemistry, since it allows a fine control of chemical bond forming and breaking processes. This opens energy efficient or selective chemical processes. For the optimal design of catalysts, a fundamental atomic scale understanding of the structure and electronic structure of the catalytic particle, in interaction with the support and with the reactant is of utmost importance. A second complementary key aspect concerns the molecular reaction mechanisms at the active site. Computational chemistry is today a key method, among other physical chemistry characterisation tools to reach such an understanding at the molecular level of the structure of the active site and of the elementary processes occurring during the catalytic act.

In the first part of the lecture, we will focus on the nature of the surface of a metal catalyst, under a pressure of gas at a given temperature. In the recent years, the combination of DFT calculations and thermodynamic approaches allowed the understanding or prediction of the nature of the most stable surface of catalysts in specific reaction conditions, giving insights very complementary to in situ characterization methods. Examples of formation of a surface carbide on various transition metals will be presented in the framework of selective hydrogenation (1,2) or Fischer-Tropsch synthesis (3).

We will then move from extended surfaces to small Pt particles (of size 1 to 13 atoms) on a α-alumina support. We show that the presence and the chemical nature of the support surface strongly impact the stability and the shape of the particle (4). More specifically, the presence of chlorine on the (110) surface of α-alumina stabilizes small platinum clusters. This stabilization originates from the simultaneous migrations of chlorine atoms and protons from the support towards the Pt clusters. In particular, this trend leads to a local energy minimum, as a function of cluster size, for the Pt3 cluster. The shape of the particles is not only affected by the support, but also by the reactants. When submitted to a pressure of hydrogen, a Pt13 particle on alumina yields a much stronger adsorption of hydrogen compared to an extended surface hence leading to a high H coverage (up to 3 H/Pt) and the formation of a surface hydride (5). Hydrogen uptake is associated with a change of the shape of the cluster and a weakening of the cluster/support interaction.

The final part will concern molecular reactivity. The mechanism of the hydrogenation of butadiene will be presented and we will show how modelling can explain why Pt is not selective for these reactions, while the PtSn alloy is (6,7). New C-H bond formation pathways, where the C=C bond is not coordinated to the surface, play a central role for the specific selectivity of the alloy.

References

1. D. Teschner, Z. Révay, J. Borsodi, M. Hävecker, A. Knop-Gericke, R. Schlögl, D. Milroy, S. David Jackson, D. Torres, P. Sautet, Angew. Chem. Int. Ed. 47 (2008) 9274
2. D. Torres, F. Cinquini and P. Sautet, J. Phys. Chem. C in press (2013), DOI: 10.1021/jp400059m
3. E. de Smit, M. M. van Schooneveld, F. Cinquini, H. Bluhm, P. Sautet, F. M. F. de Groot and B. M. Weckhuysen , Angewandte Chemie International Edition, 50, 1584 (2011)
4. C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet and P. Raybaud, ACS Catalysis 2, 1346 (2012)
5. C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet and P. Raybaud, ChemCatChem 3, 200 (2011)
6. F. Delbecq, D. Loffreda, P. Sautet, J. Phys. Chem. Lett., 1 (2010) 323-326
7. F. Vigné, J. Haubrich, D. Loffreda, P. Sautet, F. Delbecq, J. Catal. 275, 129 (2010)

DEACON CHEMISTRY REVISITED: NEW CATALYTIC PROCESSES FOR CHLORINE RECYCLING

by Javier-Perez Ramirez, ETH, Zürich, Switzerland

The heterogeneously catalyzed oxidation of HCl to Cl_2 comprises a sustainable route to valorize HCl-containing streams in the chemical industry. Conceived by Henry Deacon in 1868, this reaction has suffered from many sterile attempts to obtain sufficiently active and durable catalysts. The Deacon process has been rejuvenated in the last decade due to the increased demand for chlorine and the growing excess of by-product HCl, for example in the manufacture of polyurethanes and polycarbonates. Intense research efforts have culminated in the recent industrial implementation of RuO_2-based catalysts for HCl oxidation, and other systems based on cheaper metals are ready for commercialization. This lecture reviews the new generation of technologies for chlorine recycling under the umbrella of Catalysis Engineering, rationalizing the catalyst and reactor selection in relation to the overall process. Bridging fundamental understanding of the catalyzed reaction at the nanoscale with process scale-up was vital for research to flourish into large-scale application. Accomplishing this ambitious objective was only possible through a strong collaborative relationship between academic and industrial scientists.

References

Hevia et al., J. Catal., 2010, 276, 141.
Mondelli et al., ChemCatChem, 2011, 3, 657.
Pérez-Ramírez et al., Energy Environ. Sci., 2011, 4, 4786.
Mondelli et al., Chem. Commun., 2011, 47, 7173.
Teschner et al., J. Catal., 2012, 285, 273.
Teschner et al., Nature Chem., 2012, 4, 739.
Amrute et al., J. Catal., 2012, 286, 287.
Farra et al., J. Catal., 2013, 297, 119.
Moser et al., Appl. Catal. B, 2013, 132-133, 123.

CFD MODELING OF FLOW, MIXING AND REACTION

by Rodney Fox, Iowa State University, USA

Computational fluid dynamics (CFD) is now widely used in chemical reaction engineering to model complex single- and multiphase reacting flows. Over the past twenty years ago considerable advances have been made on several fronts (e.g. computing resources, algorithms, conceptual models, etc.), which have allowed us to increase significantly the accuracy of existing CFD models as well as to develop new models for even more complex flows. For example, twenty years most CFD simulations were done for single-phase non-reacting flows and the emphasis in research was to include realistic reaction schemes coupled to turbulent mixing in widely used reactor geometries such as stirred tanks. In the past ten years, academic and industrial CFD research has progressed to treat more and more complex reactors such as polydisperse multiphase reacting flows. The shift from single-phase flows, to which standard CFD software and algorithms can be directly applied, to multiphase flows has forced us to develop novel simulation algorithms for treating polydispersity (e.g. particle size distribution, inertial particles, etc.), many of which are not yet available in standard CFD codes (commercial or open source). In this talk, I will describe the current state of the art in CFD models for polydisperse reacting multiphase flows in the context of chemical reaction engineering. Particular attention will be paid to recent advances in quadrature-based moment methods and kinetics-based finite-volume methods.

MULTISCALE SIMULATION OF CHEMICAL REACTIONS AND REACTORS: COMBINATORIAL COMPLEXITY, UNCERTAINTY, AND EMERGENT BEHAVIOR

by Dionisios Vlachos, Department of Chemical and Biomolecular Engineering, Center for Catalytic Science and Technology and Catalysis Center for Energy Innovation, University of Delaware, Newark, USA

Multiscale simulation is a rapidly growing scientific field in chemical, materials, and biological sciences. The obvious goal of multiscale modeling is to predict macroscopic behavior of an engineering process from first principles (bottom-up approach). However, nanotechnology imposes new challenges and opportunities (top-down approach). For example, miniaturization of microchemical systems for portable and distributed power generation imposes new challenges than conventional scale-up. While major progress in multiscale modeling and simulation has recently been achieved, many important problems exhibit combinatorial complexity in parameters (e.g., in developing large reaction mechanisms), an emergent behavior in catalytic activity, and complex collective behavior. In addition, the inherent uncertainty in parameter and models makes predictions of multiscale modeling less reliable. In this talk, we will address the aforementioned issues and present examples from biomass processing and hydrogen production for portable power generation.

COILED FLOW INVERTER - NOVEL DEVICE FOR PROCESS INTENSIFICATION

by Krishna Nigam Indian Institute of Technology (IIT),
New Delhi, India

Flatter Velocity profile and more uniform thermal environments are extremely desirous factors for improved performance in flow reactors and heat exchangers. One means of achieving it in laminar flow systems is to use mixers and flow inverters. In the present study a new device is introduced based on the flow inversion by changing the direction of centrifugal force in helically coiled tubes. The main mechanism generating the flow is the production of spatially chaotic path by changing the direction of flow using a 90° bend in helical coils. In helical flow a 90° shift in the direction of centrifugal force cause a complete flow inversion. Residence Time Distribution (RTD) experiments were conducted over wide range of process parameters to study the mixing performance of the proposed device. Considerable narrowing of RTD was observed under both the conditions of significant and negligible molecular diffusion. It is interesting to mention that the first element of tracer comes out at 0.86 of mean residence time under diffusion free conditions and under significant molecular diffusion the value of Dispersion Coefficient is of the order of 0.001.

Based on the success of this innovative device its performance as a heat exchanger was also tested on pilot plant scale. The results show that even at low Reynolds numbers, heat transfer is 25% higher in Coiled Flow Inverter while pressure drop is 5-6% as compared to coiled tubes.

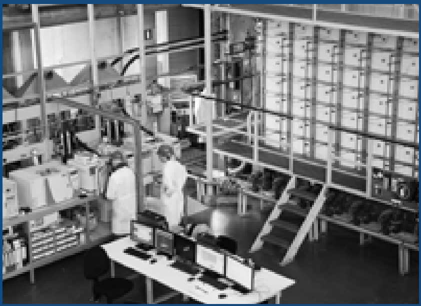
Experimental studies were also performed in Shell and Tube as well as Plate type heat exchangers on pilot plant scale while considering same heat transfer area and process conditions as Coiled Flow Inverter. It was observed that the enhancement in heat transfer in terms of the fully developed Nusselt numbers for Coiled Flow Inverter is 57-64% as compared to Shell and Tube heat exchanger while the increase in pressure drop in terms of friction factor for Coiled Flow Inverter is 25-54%. Heat transfer enhancement in Coiled Flow Inverter as compared to Plate type heat exchanger is 27-41% with increase in pressure drop of nearly 19-23%.

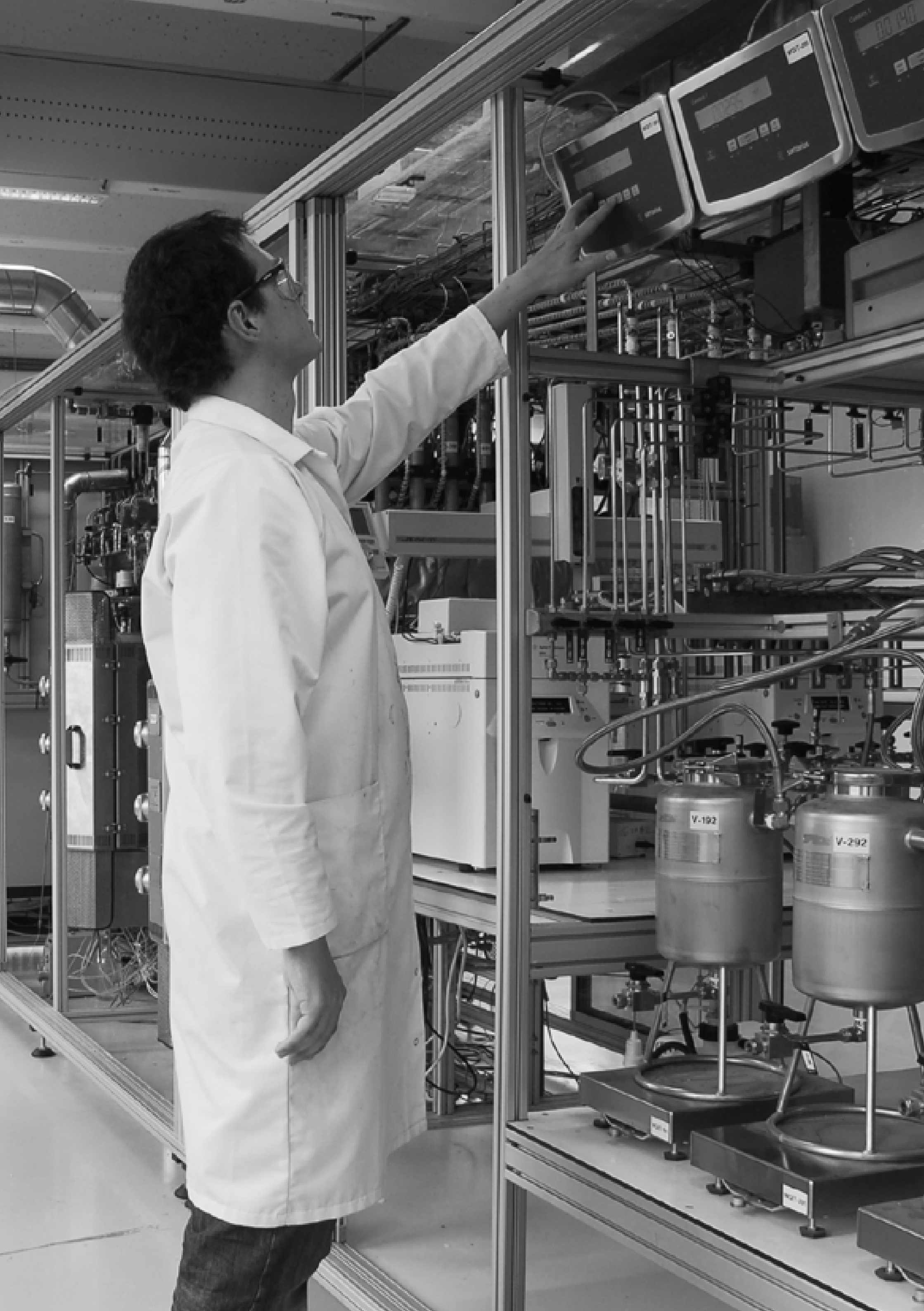
Recently, numerical investigation of the free radical polymerization of styrene in the Coiled Flow Inverter was performed using CFD-ACE 8 software. The results show that Coiled Flow Inverter has higher degree of polymerisation as compared to straight tube even at low Reynolds number. It was also observed that Coiled Flow Inverter can be used as microfluidic reactor which can help in achieving a better control over the free radical polymerization.

INAUGURATION CEREMONY OF THE RENOVATED BUILDING OF THE LABORATORY FOR CHEMICAL TECHNOLOGY

Prof Paul Van Cauwenberge, Rector of Ghent University, prof Luc Moens, vice rector of Ghent University, Prof Rik Van de Walle, Dean of the Faculty of Engineering and Architecture, Vice-Rector Luc Moens and Prof Guy Marin, Director of the Laboratory for Chemical Technology would like to invite you to attend the inauguration of the renovated building 914.

YVES CHAUVIN, Nobel Prize Chemistry 2005,
will honour us with his presence.

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