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Editorial

Reaction and Catalysis Engineering – A multi-scale, integrated approach

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This third volume of *Perspectives in Reaction Engineering and Catalysis* presents articles by world experts on various aspects that are essential for the intensification of chemical processes. These perspective articles demonstrate that rigorous modelling of the reaction kinetics of increasingly complex systems, and of non-uniform multiphase transport phenomena, as well as the inclusion of transients and dynamics, is not only gradually becoming possible, but is indispensable for improving reactor design relevant to industrial practice. Key is to *integrate* these insights, and to use a systems approach that incorporates an accurate, fundamentally rooted representation at all length and time scales. The message here is that complexity can be modelled, and can be exploited by design, but this requires rigour in the multi-scale modelling approach. In addition, instrumentation that is capable to measure properties under relevant process conditions is essential to guide process analysis and design.

Froment reviews kinetic modelling and, in particular, the single-event approach to chemical kinetics of complex processes, which he pioneered. All too frequently, he argues, kinetic models are still oversimplified. Detailed, more realistic models are required, which is challenging but achievable for industrial processes dealing with complex feedstocks that react via complex reaction networks. For catalytic processes, the detailed nature or configuration of the active catalyst site should be introduced into the kinetic equations, he argues, which is becoming possible today thanks to quantum chemical calculations. *Froment* notes that kinetic constants are more than fitting parameters, and have to satisfy physicochemical criteria. The single-event approach, based on first principles, drastically reduces the number of parameters requiring experimental determination, by accounting for the effect of structure on the frequency factor in the rate coefficient, and by relating the activation energy to the reaction enthalpy via the Evans-Polanyi relationship. Such detailed modelling is becoming practical, as more detailed chemical composition data are becoming available, thanks to improved analytical methods, as well as molecular reconstruction from global information, using

stochastic techniques. In the paper, progress in kinetic modelling is illustrated using examples from refinery and petrochemical processes. For example, for the very complex process of VGO hydrocracking, the single-event approach reduces the number of independent parameters to be determined experimentally to only 33, even though there are 126 million elementary steps on acid sites. Catalyst deactivation by coking requires a fundamental kinetic approach as well.

Smadbeck and Kaznessis discuss recent advances in modelling reactive chemical systems away from the thermodynamic limit. They note that these approaches are most relevant to biomolecular systems, for which modelling the reaction kinetics, using ordinary differential equations, will likely result in erroneous conclusions, and for which stochastic models that account for the randomness of small reacting systems are better suited. The importance of developing modelling approaches to study systems away from the thermodynamic limit has been recognized for more than 50 years, and a chemical master equation (CME) has been developed that models the randomly evolving molecular populations. However, because of its overarching character, the CME remained unsolved for years for all but the simplest of molecular interaction networks. *Smadbeck and Kaznessis* detail their efforts leading recently to the solution of the CME, particularly their zero information closure (ZI-closure) scheme that finds the lower order moments by maximizing the information entropy of any reaction network and leads to significant reductions in computational complexity and intensity. *Smadbeck and Kaznessis* provide an example of the application of their technique to a simple reaction scheme, the so-called Schlögl reaction network model. They argue that their novel technique to solve the CME will aid researchers in modelling small chemical reaction networks in a manner that is amenable to analysis and design. In particular, their approach makes it feasible to carry out parameter sensitivity and stability analysis of stochastic reaction networks, thus enabling the design of control systems for complex, nonlinear networks of reactions away from the thermodynamic limit. Of particular value may be the application of their ZI-closure approach in identifying components and interactions for synthetic biological systems, thus allowing modelling to play an increasingly important role in biological engineering.

Fundamental modelling approaches are equally important to describe transport phenomena – the interface between the microscopic scale of chemical kinetics, and the macroscopic reactor scale. The dynamics of dense fluid-particle systems, while prevalent in industrial processes, remain difficult to simulate. *Deen and Kuipers* present two examples of the power of Direct Numerical Simulations (DNS) to parameterize coarser-grained models, as part of a multi-scale simulation framework. In a first example, they apply DNS to calculate the closure for fluid-particle drag in a binary particle mixture; the drag force correlation derived from DNS is substituted in Discrete Element Modelling (DEM) equations that are used to simulate rates of segregation in a gas-solid fluidized bed. In a second example, DNS is used to predict the distribution of the fluid-particle heat transfer coefficient in a dense, random array of particles; even though the average agrees well with Gunn's correlation, variations around the average are quite large. There are still many challenges, such as the incorporation of chemical reactions, especially for porous catalysts with internal transport limitations, or the extension to non-spherical particles.

Structured catalysts, in the form of honeycomb monoliths, became commercial in the early 80's for automotive emissions control and for NO_x reduction from power plants. Substantial efforts have been devoted since to their adoption for other reactions, motivated by the prospect of lower pressure drops and smaller reactor volumes as compared to conventional catalyst pellets. Despite the initial promise and all good efforts since, the use of catalytic monoliths is still limited today to the original environmental applications. *Tronconi* notes that

this is because many other applications are plagued by one of the following issues: (i) the smaller amount of catalyst in wash-coated monoliths, compared to pellets, leading to lower conversions for kinetically limited processes, and (ii) the adiabatic nature of conventional parallel channel ceramic monoliths, which hinders temperature control for endo- and exothermic chemical processes, where effective heat exchange is crucial. *Tronconi* reviews recent efforts to overcome the second challenge; specifically, the use of conductive honeycomb monolith catalysts, metallic open-cell foams, and metallic microfibrinous entrapped catalysts. Such engineered systems facilitate heat management of strongly exo- or endothermic catalytic processes via heat conduction in their thermally connected structure. Two important reactions are receiving particular attention, namely Fischer-Tropsch synthesis and catalytic partial oxidations. *Tronconi* concludes his paper by pointing out the need for larger-scale demonstrations in order to address practical aspects relevant to commercial application, e.g., loading, sealing and unloading of the monoliths or foams in the reactors, and validating their economical, operational advantage in view of higher catalyst manufacturing and development costs.

Another way to intensify processes is to use electromagnetic radiation. Microwave and photocatalytic reactors hold great promise, but are not used commercially as often as could be expected from their process intensification potential. *Lakerveld, Sturm, Stankiewicz and Stefanidis* point out why, and propose routes to change this. Process design should follow an integrated approach, including the electromagnetic energy source (microwave or light generator), reactor configuration, and catalyst. There is room for novel reactor development, such as the travelling wave reactor, to achieve highly controlled and optimized microwave conditions. Various microwave frequencies, different from the conventional 2.45 GHz should be explored. Instrumentation is required to measure, e.g., the dielectric properties of catalysts, temperature in the presence of a microwave field, or sensors that measure electric field intensity, all under real process conditions. Design and control strategies are lacking. For photocatalytic reactors, LED arrays offer opportunities for improved design of the radiation field, and dynamic aspects of LED illumination could be exploited.

Hydrogen is considered today a potential alternative to hydrocarbon-based fuels via its use in fuel cell powered vehicles. *Hwang and Varma* in their paper note that a major obstacle hindering the further development of these systems is the lack of safe, light-weight and energy-efficient on-board hydrogen storage systems. Their paper provides a concise review of efforts over the last couple of decades to develop effective hydrogen storage methods, including tanks, sorbents, and metal and chemical hydrides. *Hwang and Varma* review the current status of development for each of these storage technologies, explain their advantages and disadvantages, and provide their perspective of what lies ahead for each of these systems. They conclude their paper by noting that for hydrogen to find broad use in vehicular applications, along with key material discoveries, efforts must also be made in optimizing overall system performance. In addition, a better understanding of the relationship between cost, energy efficiency and environmental impact for the various approaches is necessary in order to address life-cycle issues for each of these systems.

Catalytic partial oxidation (CPO) and oxidative dehydrogenation (ODH) are becoming today attractive technologies in the USA for the production of various chemical intermediates, due primarily to the explosive growth of shale-gas production. And though these processes share common features with other common highly exothermic reactions, there are also fundamental differences that result from their very high temperature of operation and the very short contact times required. *Balakotaiah and West* in their paper note that it is these key differences for CPO and ODH that dictate during reactor design the careful consideration of all

the accompanying thermal effects and the undesired catalytic and/or homogeneous side reactions that they could trigger. In particular, they indicate that it is essential for the reactor designer to understand the various ignitions and extinctions that may take place and the associated transients that could occur. *Balakotaiah and West* present a concise overview of the various bifurcations that one may encounter, and their impact on optimal reactor design and on the yield to desired products.