MARC-OLIVIER COPPENS

Nature Inspired Chemical Engineering: A New Paradigm for Sustainability

Our society is faced with urgent challenges related to increasing energy efficiency, extending access to clean and fresh water and air, and making chemical processes more selective and environmentally acceptable. Chemical engineering is ideally positioned for presenting technological advances in these areas, and they should be considered in the economical, but also the social, political, legal and cultural contexts that define viable implementations. Each of these aspects is important for sustainable development.

Professor Marc-Olivier Coppens
Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute, USA
coppens@rpi.edu
CAS Fellow 2007/2008

Tremendous progress has been made in our ability to manipulate matter on ever-smaller scales and to make accurate supporting measurements that allow us to spatially resolve structures and to follow molecular transport and reaction dynamics. Combined with theoretical scientific advances, increasing computational power, and better computer algorithms, the road is, in principle, open for the rational design of new products and processes that could address the above-mentioned issues. While advances in micro- and nanotechnology might help to synthesize these designs, the challenges remain huge because of the large gap between atomic and macroscopic scales and an enormous gap in time scales. For example, there are ten orders of magnitude (10^{10}) between the size of an atom and one meter, and twelve (10^{12}) or more between the period of an atomic vibration, and the seconds, hours or years that are relevant to macroscopic chemical processes. On the other hand, the overall phenomenological, largely empirical models that have up to now been at the basis of most chemical process and product engineering are untenable, as they likely lead to inefficient, sub-optimal designs, and offer only incremental progress, rather than leading to the required radical innovations.

We propose to learn from nature as a fertile ground for transformative innovations. Nature has frequently been a source of inspiration for artists and scientists alike [1, 2]. In catalysis, for example, the selectivity of biological catalysts (enzymes) for carrying out specific chemical reactions at temperatures close to room temperature is remarkable compared with that of typical chemical (heterogeneous) catalysts, which also typically require much higher temperatures to be active. The geometrical and chemical structure of enzymes has therefore been imitated in the design of biomimetic catalysts that employ a similar lock-and-key mechanism to selectively carry out a desired chemical reaction. The multi-scale structure of microscopic hairs (setae), splitting into nanoscopic spatulas on gecko

feet has recently inspired very strong carbon nanotube-based adhesives, using a similar hierarchical structure [3]. Likewise, the hierarchical structure of self-cleaning lotus leaves has inspired the design of water- and dirt-repellent coatings. However, when it comes to chemical engineering, the difference between nature's ways of carrying out a physicochemical process and the engineer's solution is striking. Certainly, engineers have the ability to employ different materials, and they have access to different operating conditions, such as high temperatures and pressures, which biology does not have at its disposal. This could increase the (thermodynamic) efficiency of certain processes, although even here the question of effectiveness in terms of life cycle analysis remains, e.g. the formation of non-degradable or recyclable side products and safety issues. Blind imitation of nature's solutions will not typically lead to the best solutions. Ignoring nature's solutions, however, means missing clues to very efficient and effective ways to bridge multi-scale gaps, which is one of the engineer's most difficult problems: How can an improved design at the nano- or micro-scale be translated to the macroscopic dimensions required in many applications? For example, fluid motion in a lab-scale process differs from that in the large reactor vessels that are typically used for chemical production, affecting overall performance and product selectivity, and possibly presenting safety hazards. Despite considerable progress in fluid mechanics simulations, the model-based scale-up of multiphase reactors (involving gases and liquids or solids) is a challenging problem. Because such reactors are used in some of the most important processes for fuel and chemical production, more robust, scalable designs are highly desired.

Trees and lungs hold clues to solve this problem. More generally, nature presents attractive solutions to the bridging of multi-scale gaps, typically by means of fractal geometry. Fractals are structures that look similar at multiple length or time scales. Examples include trees, lungs, river basins, mountain ranges, natural coastlines, and the vascular network. Magnifying a small part of these objects brings up images that are indistinguishable from larger parts, within a certain range of scales: the fractal scaling range. Mandelbrot first presented the common mathematical framework for these diverse objects, coining the word "fractal" to describe them [4]. Mathematical fractals, such as Cantor sets, Koch curves and Sierpinski gaskets, can be constructed to be exactly, infinitely self-similar, at all length scales; whatever the magnification, the same structure reappears. This is very different from objects in Euclidean (classical) geometry, such as circles, cones or squares, which become smooth and straight almost everywhere at sufficiently small scales. Self-similarity in nature has the same repetitive characteristic as mathematical fractals, making fractal geometry the "natural" language within this scaling range, but it breaks down at some finite scale (e.g. that of atoms or basic constituting particles, like individual cells) and it is stochastic, i.e. the similarity from one scale to another is to be viewed in a statistical sense. Fractals are beautiful, but also useful. Fractality implies symmetry, namely invariance under magnification, just like translational or rotational symmetry represents invariance under displacement or turning. Because of this, discovering a fractal structure enables us to describe a structure with much less information than through the language of classical geometry. Importantly, also *imposing* a fractal structure is a powerful simplification, often leading to very desir-

able features. It is this simplification – the ability to bridge multi-scale gaps – that can be exploited by rational fractal design over an optimal range of length or time scales.

A tree, whose branching crown and root network are fractal, grows in a self-similar way, and effectively bridges scales between the leaves and the trunk. The size of the twigs and the leaves is not related to the overall size of the tree; only the number of branching generations of the tree crown increases when the tree grows. Its desirable mechanical properties were already noted by the architect Gaudí, who utilized tree-inspired columns to support his famous *Sagrada Familia* cathedral in Barcelona. Gaudí was convinced that nature's designs are the most economical and long lasting. But a tree crown is also effective in preserving the same chemical reactions at the level of the leaves, irrespective of tree size. A tree can be viewed as a photosynthesis reactor, converting carbon dioxide and water into biomass (the growing tree) and oxygen. Similar arguments can be made about the lung. The branching structure of an adult human lung connects the bronchioles and the trachea via a self-similar structure over 14–16 generations [5]. The architecture of the lung was also shown to lead to minimal entropy generation, which is equivalent to the highest thermodynamic efficiency for air transport [6]. Such fractal structures of channels are effective fluid distributors and collectors, connecting a huge volume and surface area to a single point. This concept led us to propose a fluid distributor, the so-called *fractal injector*, which distributes gas or liquid uniformly over a large reactor volume from a single inlet [7]. The fluid leaves the injector via outlets at the deepest generation (the "twigs"), which are equidistant to the inlet, resulting in equal pressure drops from the inlet to each of the outlets, and uniform flow. The low pressure drop saves energy. In a small reactor, the distributor only has one or two generations of branching tubes. In a larger reactor, generations are added, conserving the size of the outlets and the distance in between. This differs from conventional reactor design, in which larger tubes are used to distribute fluid over larger reactor vessels, with often empirically determined outlet position(s) and added baffles or mixers to compensate for scale-dependence. It is quite similar, however, to botanical trees and to other natural distribution and collection networks like lungs, in which the smallest size (twigs, leaves or cells) is maintained with age or overall size, while the interpolation between small and large scale occurs via a self-similar fractal network whose number of generations increases with size [2]. Such designs could be applied not only to three-dimensional reactor vessels, but also to spread a fluid in the two-dimensional plane, like a shower cap over a column containing a medium that needs to be uniformly irrigated. The latter, using area-filling branching, has been applied in the context of distillation and chromatography [8]. It could also, as we suggested while working at the Center for Advanced Studies, be employed to distribute fuel or oxygen over a fuel cell.

Observing biological reactors and separation devices, such as trees and lungs, we frequently notice a change in structure below a certain length scale, corresponding to a change in the underlying dominating transport and molecular exchange mechanisms. Once again, structure and function are related. The venal architecture of leaves tends to become uniform at small length scales, approaching those of the cells that house the photosynthetic complex. Below the level of the bronchioles, the pulmonary

structure is more compact: acini, lined by alveoli (which exchange oxygen and carbon dioxide with the surrounding blood vessels) are somewhat akin in their geometry to bunches of grapes. Diffusion, rather than flow, is the dominating transport mechanism at those small scales, and the walls are flexible and permeable.

This inspires novel designs for solid porous catalyst particles. Catalysts are used to increase the rate of chemical reactions and to enhance the selectivity toward desired compounds in industrial production, environmental and energy-related processes. By using solid catalysts, traversed by a vast network of nanometer-sized pores that provide access to the "active sites" on which the catalytic reactions take place, huge catalytic activity per unit of volume can in principle be achieved. However, because these nanopores are so narrow, molecular transport via diffusion through them is slow, hence it is desirable to introduce large pore channels as "highways" to increase the overall, effective activity, and to limit catalyst de-activation by pore blockage. The optimal distribution of large channels is found to depend on the boundary conditions. Mathematical optimization shows that, for a large number of channels and uniform distribution of reactants from the boundary of the catalyst particle, the highest yield is obtained for large channels of an optimal size, with an optimal thickness of nanoporous material in between the channels [9, 10]. In the molecular diffusion-controlled regime, a uniform, rather than a fractal structure emerges, but this optimum is changed when flow is the dominating transport mechanism, or when overall robustness or other criteria are set as objectives.

These examples illustrate a common paradigm to achieve more efficient chemical processes and materials, summarized in Figure 1: biological structures are an excellent source of inspiration for engineer designs that bridge multiple length scales, maintaining efficiency under scale-up. At the

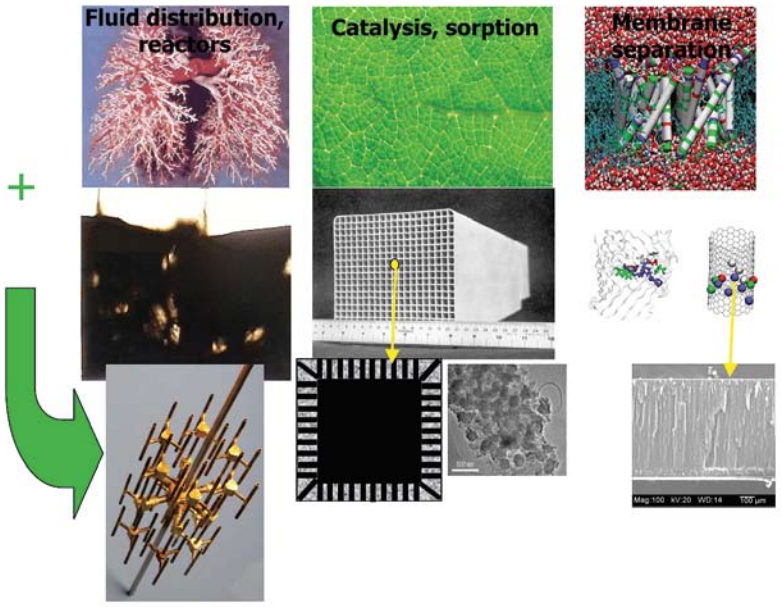

Figure 1: Multiscale nature-inspired chemical engineering. Left: fractal fluid distributors for multiphase reactors, inspired by the structure of the lungs and vascular network. Middle: design of hierarchical catalyst pore networks, inspired by the venal architecture of leaves. Right: design of membranes for high-flux highly selective separations, inspired by protein channels in cell membranes.

smallest scales, the structure is very specific, and dependent on the intrinsic function. At intermediate scales, uniform arrays appear common. At larger scales, fractal interpolation is very powerful to preserve the desired functionality. Other examples of nature-inspired chemical engineering include membranes for separation processes that imitate the key features of protein channels traversing cell walls, in order to achieve high flux and selectivity [11]. Employing a lung-like structure at larger length scales might be advantageous for creating robust, high-capacity devices, although this remains to be demonstrated.

The influence of dynamics has not been discussed, but is known to be essential to life. Chaotic systems can be dynamically perturbed to behave in a more ordered way using low energy input, and to realize steady states unachievable under static conditions. This opens the way to new classes of engineering designs that explicitly employ dynamic perturbations. Finally, it is the combination of bottom-up atomistic modeling, advances in mesoscopic theory and statistical physics, with more holistic methodologies such as chaos theory and fractal geometry that can help us to better understand, model and design systems, while considerable advances in material synthesis (self-assembly, structure-direction by templating and other means, micromachinery, etc …) help us to build them.

References

[1] Y. Bar-Cohen (ed.), 2005, *Biomimetics: Biologically Inspired Technologies*. Taylor & Francis.

[2] M.-O. Coppens, 2003, *Nature Inspired Chemical Engineering*. Delft University Press.

[3] L. Ge, S. Sethi, L. Ci, P.M. Ajayan, and A. Dhinojwala, 2007, Carbon nanotube-based synthetic gecko tapes. *Proc. Natl. Acad. Sci.* 104, 10792–10795.

[4] B.B. Mandelbrot, 1982, *The Fractal Geometry of Nature*, Freeman, San Francisco

[5] E.R. Weibel, 1984, *The Pathway of Oxygen*. Harvard University Press. Cambridge, MA

[6] S. Gheorghiu, S. Kjelstrup, P. Pfeifer and M.-O. Coppens, 2005, Is the lung an optimal gas exchanger? In: *Fractals in Biology and Medicine*. G.A. Losa, D. Merlini, T.F. Nonnenmacher and E.R. Weibel (eds.), Springer Verlag, Birkhäuser Basel, 31–42.

[7] M.-O. Coppens, 2005, Scaling up and down in a nature inspired way. *Ind. Engng Chem. Res.* 44, 5011–5019.

[8] M.M. Kearney, 2000, Engineered fractals enhance process applications. *Chem. Eng. Prog.* 96, 61–68.

[9] G. Wang and M.-O. Coppens, 2008, Calculation of the optimal macropore size in nanoporous catalysts and its application to DeNOx catalysis. *Ind. Engng Chem. Res.* 47, 3847–3855.

[10] E. Johannessen, G. Wang, and M.-O. Coppens, 2007, Optimal distributor networks in porous catalyst pellets. I. Molecular diffusion. *Ind. Eng. Chem. Res.* 46, 4245–4256.

[11] M.-O. Coppens and A.J. Dammers, 2006, Effects of heterogeneity on diffusion in nanopores – From inorganic materials to protein crystals and ion channels. *Fluid Phase Equil.* 241(1-2), 308–316.