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Process Intensification and Process System Engineering: a friendly Symbiosis

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Process Intensification, is it a research area or a set of objectives [1]? In our view it is both. Process Intensification (PI) is an area in the discipline chemical engineering; taking the conventional, existing technologies as a frame of reference, it tries to achieve drastic improvements in the efficiency of chemical and biochemical processes by developing innovative, often radically new types of equipment, processes and their operation.
One could argue that such objective and objects of study are the hallmark of chemical engineering for many decades. Figure 1 shows a striking similarity of plants in the past and in modern times, in spite of a gap of many centuries. It underlines the feeling that there might be room for breakthroughs in plant design. Conceptually, PI belongs to the discipline of chemical engineering but compelling examples suggest that there is something as a "PI approach" that gives it the character of a research area.

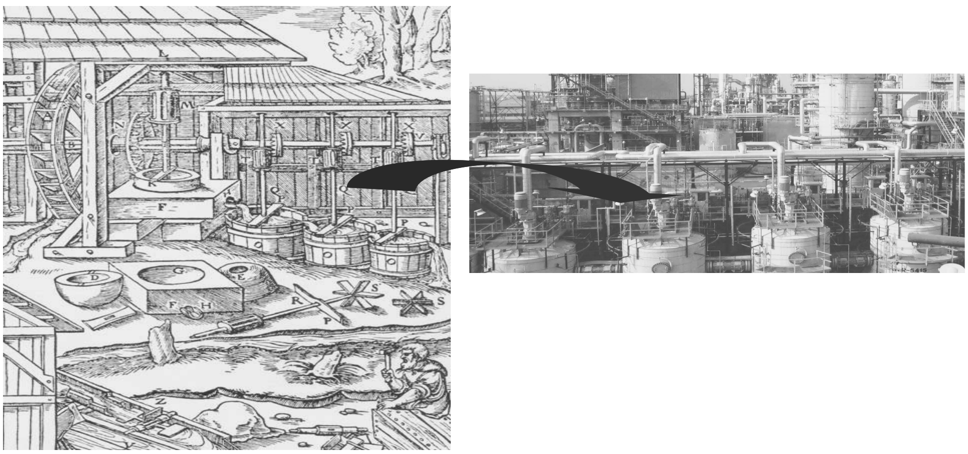

Figure 1. The modern plant is not that modern…

Miniaturization of the plant or integration of reaction and separation within one zone of the apparatus, have become a hallmark of Process Intensification. But PI has also other sustainability-related dimensions, such as significantly increased material efficiency, reduced energy usage, reduced waste generation and increased process safety. Producing much more with much less is the clue to Process Intensification. It provides a new avenue to a better economy and ecology of industrial production clusters.

Essential for Chemical Engineering is that it is a *multi-scale* (in space and in time) discipline. Traditionally, three spatial scales are considered, the *process*, the *process unit* and a *compartment* within a unit. The more refined scales are treated as part of the compartment in a lumped manner for reason of conciseness. The question then arises at what scale does PI takes place. In a top-down approach one might limit PI to the meso (process unit) and macrolevel (process). So, given the chemistry and physics, the chemical engineer designs the optimal intensified process. However, it is more rewarding to consider more scales. At the *upper level of aggregation,* the supply chain should be the reference level for setting life span oriented performance targets for an intensified plant; at the lower *level,* the molecules and catalytic sites are obviously instrumental in enabling the goals of PI. The particle and the intraparticle space are considered to belong to the mesolevel.

What is a good strategy for PI? Miniaturisation and increased resource efficiency can be achieved by enhancing the target rate processes by an order of magnitude, while suppressing the rates of competing phenomena. Since there are many different, up to now unexplored ways to do so, it will be clear that the philosophy of PI (PI, what it is and how it can be done, what are the drivers?) is not yet mature and, as a consequence, examples are crucial. The lecture will focus on examples from chemical and biochemical processes and from these examples contributions to theory will be formulated. Contributions can be in the field of *hardware*, e.g., structured catalysts and reactors, and *methods*, e.g., (bio)reactive or hybrid separations. In a sense this division is analogous to that of IT in *hardware* and *software*.

In the world of *hardware* high performance reactors and column internals have received most attention. A classical example of the former is the structured reactor. Structured reactors have fascinating characteristics. They enable high rates and selectivity. Figure 2 shows that at the same power input the mass transfer (G-L) in monolithic reactors under conditions of so-called Taylor flow is one to two orders faster than in turbulent contactors. In coated reactors gas transport from the gas phase to the (catalytic) wall is essential and it appears that the dominant resistance is in the film. From simple physics it is clear that the film is thicker, the higher the velocity. So, G-S mass transfer will be highest at lowest flow rates! So, in multiphase applications in the Taylor-flow regime structured reactors enable high rates of mass transfer at laminar conditions, defying the Chilton-Colburn analogy! In conclusion, in PI structured reactors and contactors are of great value.

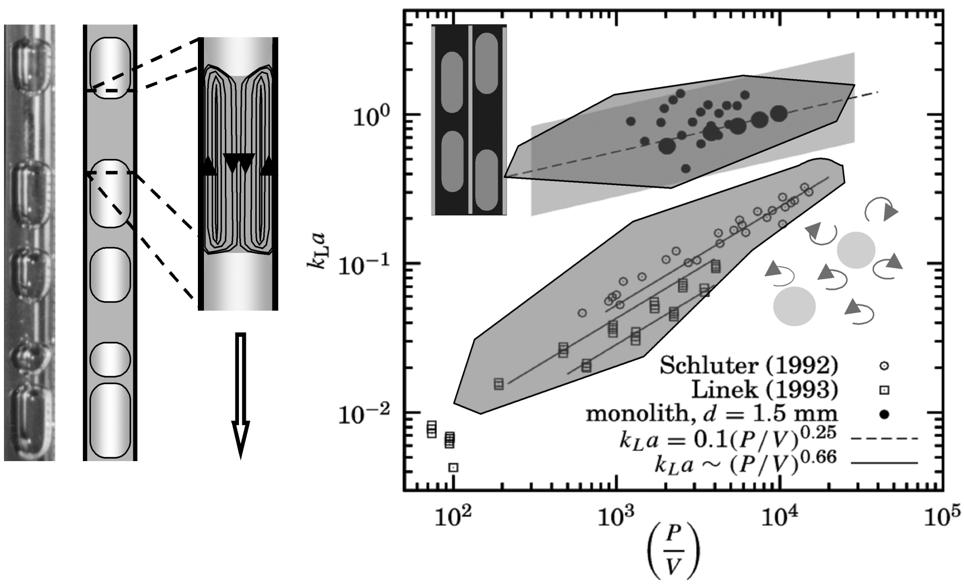

Figure 2. Taylor flow in monolithic channels results in an order larger mass transfer rates compared to stirred tank reactors

Microreactors in general are examples of structured reactors. Microreaction technology promises breakthrough technology in many areas. Here, we can learn from life sciences where microarrays play a crucial role not only in analysis but also in synthesis. Due to the high surface volume ratio microreactors have the promise of extremely high process intensification coupled with the option of high heat transfer allowing isothermal conditions, even for highly exothermal reactions. Integrated heat exchanger reactors, where the heart source and sink are in direct contact, open up new ways for PI.

Another example of intensified equipment are the structured catalytic packings, allowing the simultaneous chemical reaction and separation of the reaction products from the reaction environment (Fig. 3). It leads to the conversion enhancement, avoiding of by-products and energy saving. Later, under *methods* their functions will be discussed in more detail.

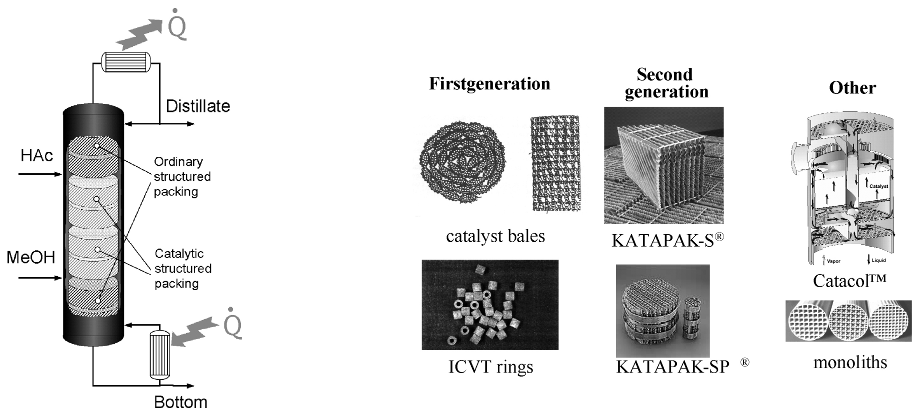

Fig 3: Catalytic distillation column (left); Examples of catalytic internals (right) [5]

Closely connected with the equipment are the materials. The operating conditions of the unit can be moved towards more extreme and favourable conditions by introducing more resistant materials for the walls and contact surfaces.

At the *methods* side a wealth of opportunities suggest themselves. Several types of functional materials are available that can have a large impact on the design of a process for a desired (bio)chemical and physical transformations. An important representative of a (functional) material is a catalyst. Catalysts perform essential functions in most chemical conversion processes, in both classical and novel applications. With respect to PI it can be worthwhile to replace random packed bed reactors by structured reactors, containing catalytic coatings. Catalytic coatings are very attractive from the point of view of maximizing selectivity. For serial kinetics when the intermediate is the desired product, the well-defined thin coatings enable unprecedented high selectivity in a convenient fixed bed reactor. It is fair to state that for a good performance of any fixed bed reactor a stable catalyst is required. In practice, for structured reactors this usually is the critical point, in particular when catalytic coatings are applied.

Alternative forms of energy, such as microwaves may accelerate chemical processes hundreds if not thousands times. Some of these alternative energy forms, such as electromagnetic or acoustic fields, allow for essentially 100% selective product formation, without any by-products, unachievable with conventional technologies, or allow for synthesis of products that could not be synthesized at all with conventional methods. The application of photons in chemical engineering provides an additional degree of freedom with potential for PI. Not surprising, catalysis is instrumental in novel processes and photocatalysis is a new fast developing field, allowing for instance artificial photosynthesis, that might even (partially) solve the Greenhouse effect. Another option is the exploitation of non-linear dynamics by means of advanced control over a dynamic mode of operation (periodic, flow reversal).

In multiphase reactors in the Taylor flow regime mass transfer is strongly enhanced by the local hydrodynamics. Many other options emerge for enhancing the key rate processes associated with the function of the unit. A classical example of utilizing a force field is the so-called Spinning Disk Reactor, which applied to an industrial, phase transfer-catalyzed Darzen reaction, resulted in 1000-fold reduction of the processing time, 100-fold reduction of equipment inventory and 12-fold reduction of the by-products level [1]. Conceptually, the Spinning Disk Reactor belongs to the category of multifunctional structured reactors.

Structuring can be done not only at the scale of the reactor, but also on the scale of the catalyst particle. This gives fascinating degrees of freedom. Good examples are membranes covering catalyst particles allowing high selectivity or pores consisting of a hydrophobic wall in an aqueous environment, enabling chemical environments that are related to the remarkable world of enzymes. This can lead to high precision, enabling in a sense PI at the source.

On the lowest scale the chemistry is dominant. Modification of the chemistry and the reaction path has the most profound effect of all, since it affects the nature and amounts of the chemical species in the units. New catalytic materials can lead to breakthroughs. Examples are multifunctional catalysts and enzymes. Many enzymes exhibit simultaneously high selectivity and high rates, providing a basis for intensified processes. Also in this case the rule holds: a superior catalyst usually deserves a structured reactor!

The integration of reaction and separation into one unit (i.e. in a single piece of equipment) or the integration of several separations leads to reactive separations or hybrid separations, respectively. The reactive distillation application in Eastman-Kodak process is one of the most striking examples for the integration of reaction and separation [1]. But such integration may also lead to some disadvantages. One of them is the necessity to operate the reaction and separation at the same pressure and temperature what reduces the degree of freedom. Also equipment design influences the operating window of an integrated process. The degree of integration of both functionalities, reaction and separation, is another parameter for process optimisation. Therefore, it has to be checked in each individual case whether integration is advantageous or not. The well established PSE tools like heuristic rules (using e.g. PROSYN), reactive distillation residue curve maps, or MINLP methods can help in finding of optimal design of reactive separation processes [6]). These tools can also be applied to find the sequencing of hybrid separations (like combination of chromatography and extraction, distillation and crystallisation, distillation and pervaporation etc.) [7, 17]. Since hybrid separations replace energy intensive separation methods for isomer separation or bioethanol production, they lead to the real PI [8]. Figure 4 gives an overview illustrating the wealth of options in combining different functions.

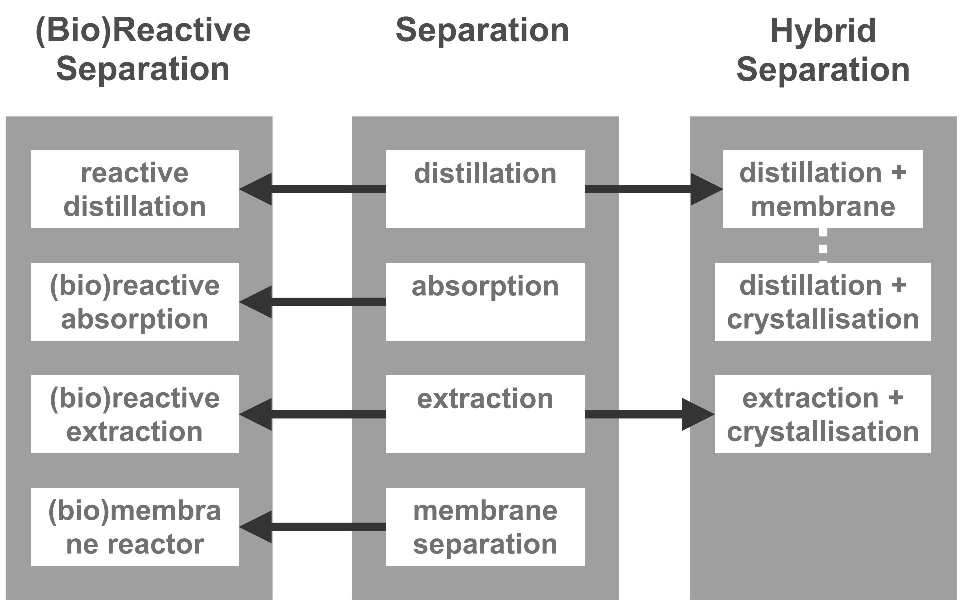

Figure 4. Separation and reaction options can be combined to multifunctional reactors and hybrid separations.

PI is important for all sectors where chemical engineering is important: from pharma to the oil refinery. A special sector is biotechnology where the systems in general are very diluted and, as a consequence, PI can contribute a lot. In-situ removal of products e.g. extraction of metabolites or adsorption of enzymes has the potential of making a revolutionary contribution. An example may be the efficient oxygenase-based whole-cell catalysis of various commercially interesting reactions such as the biosynthesis of chiral compounds [9].

Critical issues such as reaching high enzyme activity and specificity, product degradation, cofactor recycling, reactant toxicity, and substrate and oxygen mass transfer can be overcome by biochemical process engineering and biocatalyst engineering. Both strategies provide a growing toolset to facilitate process implementation, optimization, and scale-up.

A division in *hardware* and *methods* is in a sense artificial, the more so, when higher aggregation levels are considered. This may become clear from the following. At the level of the supply chain one might think of e.g. the consequences of transport of dangerous chemicals from one plant to the other. An example is the elimination of transport of phosgene. By microreactor technology small-scale on-site production can lead to PI. On the one hand, the microreactor is a piece of equipment, on the other hand it represents a novel processing method. Another example concerns functional materials. Photo-and electrocatalytic materials might be considered to belong to the category *hardware* but they are the basis of photo- and electro-catalysis, being processing *methods*.

Process Intensification significantly increases safety of chemical processes. It is obvious that smaller is safer and making inventories smaller is the first fundamental rule of the Inherently Safer Process Design. As Trevor Kletz said: "what you do not have, cannot leak" [10]. The U.S. studies showed for instance that methyl isocyanate (MIC), the poisonous intermediate that had been released at Bhopal, could have been generated and immediately converted to final products in continuous reactors containing a total inventory of less than 10 kg of MIC [11]. In reality ca. 41 tons of MIC had been released in Bhopal causing almost 4,000 deaths.

Process Intensification offers not only smaller equipment; it also offers much better possibilities for keeping processes under control. This can be done for example via extremely efficient heat removal using micro devices (heat transfer coefficients exceeding 20,000 W/m^2K) or via a fully controlled gas-liquid flow in structured catalysts, preventing liquid maldistribution and hot-spot formation. The Bhopal disaster convincingly shows the potential benefit of minimising inventories by the choice of continuous instead of batch processing. Of course, other actions could be advisable. Also high heat transfer equipment could have reduced the damage.

Let us now consider the relation between PSE and PI and the options for synergy. In PSE usually a top-down functional approach is taken. It is acknowledged that the intensification options at the upper scales have already been subject of thorough study within the PSE discipline. At the *process plant scale* the optimised use of common resources contributes to PI. The functional requirements (production capacity and quality, responsiveness to market dynamics, SHE requirements, ..) provide the reference conditions for the design of an effective network to distribute the various common physical resources in the plant (energy, exergy, solvents, water and other utilities) over the process units. Process Integration methods provide an established framework for tackling this resource issue [12]. Other concerns about critical resources at the *scale of the plant* involve the reliability and availability of the plant [13] as well as its capability to deliver on-spec product(s) [14]. Yet, at the scale of the *molecules, structure of the catalyst, sites and local fluid dynamics*, PSE has had less impact, traditionally, although it is recognized that the available PSE methods and tools can potentially have a very significant impact. In contrast, PI is very much focused on (bio)chemical engineering science aspects of the process units and the compartments within the units.

In Figure 5 it is attempted to define PI in relation with PSE. The focus and action of Process Systems Engineering takes place **along** the product creation chain [15], marked by the pink arrow, while the focus and action of Process Intensification is on the separate boxes: it has a more analytical than integrating character and primarily aims at higher efficiency of individual steps in that chain. Also the scales considered are different; PSE focuses less on the scale of molecules, sites and (nano)structure, whereas PI explicitly includes this level but often gives less attention to the highest level. It is clear that PI has consequences for the "longitudinal" action of PSE; for instance, development and application of a reactive separation can influence the PSE over the whole chain, from molecule to site, if not to enterprise.

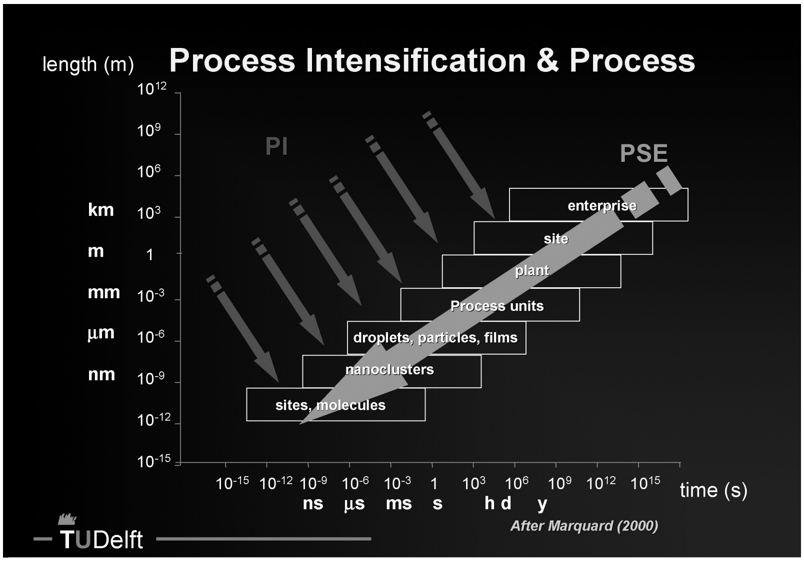

Figure 5. The relation between PSE and PI

As seen from the PSE philosophy the following points of attention for PI come forward. Process intensification, which aims at better utilisation of physical resources and an associated reduction in sizes of process equipment, is not risk free. While reduced storage of dangerous materials will greatly improve safety, the fast dynamics of the process (unit) can endanger the resiliency or stability of the process against disturbances [16]. Also, the operability and availability of the intensified process need to be investigated in order to secure the potential investment benefits by an anticipated flawless plant operation. Here a fruitful symbiosis between PSE and PI is essential. Another area for cross-fertilisation is in the application of synthesis methods (conceptual and computational) to the creation of novel processing structures at the micro-scale and below.

While an intensified plant is economically a better plant, the issue whether it is also a better plant from sustainability point of view in every respect is not entirely settled. Intensification of rate processes by coupling and strengthening of driving forces will give rise to more entropy production and exergy losses. Although it may happen that at an integrated and intensified unit the exergy losses increase relatively to a conventional base case, the exergy losses at the overall plant can decrease, due to a drastic reduction in number of transfer and separation operations, so enhancing economics and sustainability in parallel.

There might well be important open issues regarding process control: at certain conditions highly compact, intensified units may be poorly controllable or responsive to changing external conditions, like feed composition, desired product mix. What is the impact of modern smart control (e.g., new micro-scale sensors and actuators and advanced First Principles model-based control algorithms) on the optimal design of intensified plants? Are dynamic modes of operation better achievable in intensified plants? What is the impact from the option of applying more extreme conditions?

Other questions to be addressed are in the multi-scale modeling area: What is the proper process modeling depth - from short-cuts to CFD applications – for each of the considered scales? What is the necessary accuracy of measured model parameters in connection with the chosen modeling depth? How predictive are the simulation methods of intensified processes? The answer to these questions can not be given for all PI operations but some general recommendations can be formulated for reactive separations [17].

Reactive absorption, distillation and extraction have much in common. First of all, they involve at least one liquid phase, and therefore the properties of the liquid state become significant. Second, they occur in moving systems, thus the process hydrodynamics plays an important part. Third, these processes are based on the contact of at least two phases, and therefore, the interfacial transport phenomena have to be considered. Further common features are multicomponent interactions of mixture components, a tricky interplay of mass transport and chemical reactions, complex process chemistry and thermodynamics. The most important model parameters are: VLE-equlibrium, reaction kinetics and mass transfer coefficients. The modelling approaches of reactive separations are given in Fig.6
Rate-based approach must be used for the modelling of reactive absorption. The use of the equilibrium stage model is usually accurate enough to predict the steady state and dynamic behaviour of reactive distillation columns. Recently CFD may become a powerful theoretical tool to predict the flow behaviour under different column unit and internals geometries for engineering applications. In particular, it can play an outstanding role in the development of the column internals for reactive separations. The optimal complexity of the model for reactive separations depends on one hand on the model accuracy, but on the other hand on the availability of the model parameters and efficiency of the simulation methods (Fig 7).

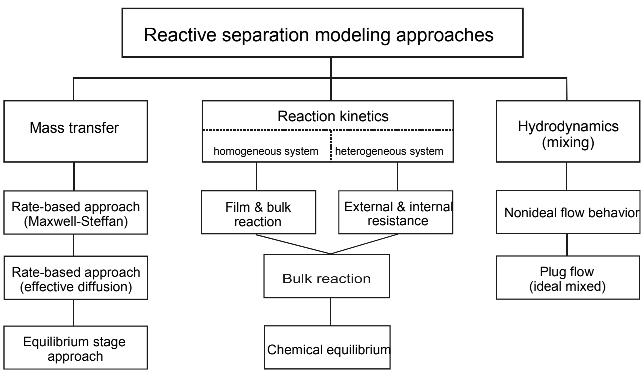

Figure 6. Modelling approaches for reactive separations [5]

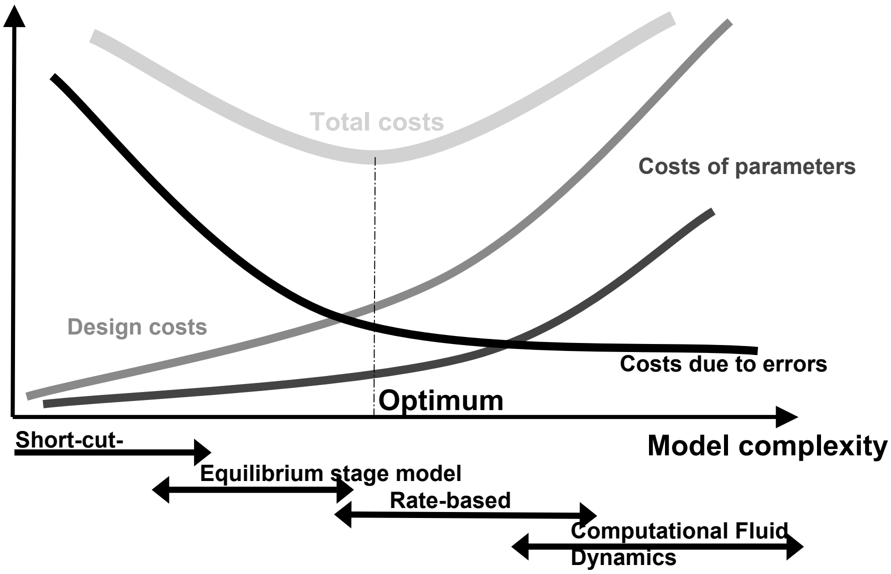

Fig 7: Design costs as a function of model complexity for reactive separations

It will be concluded that the approaches in PI and PSE are complimentary as indicated in Figure 5, indicating opportunities to intensify the interaction process between PI and PSE. The widening span of scales and the increasing diversity of processing methods call for a joint effort. A friendly symbiosis will be beneficial for innovative designs of future plants to save energy and resources, be it for the production of simple bulk chemicals, complex products, medicines or other consumer products.

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