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Phenomena-based modularisation of chemical process models to approach intensive options

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Abstract

The fundamental thinking underpinning process intensification (PI) involves an understanding of process phenomena at various levels and their interrelationships without the spatial constrains of conventional unit operation models. This paper presents a framework in which the process models are based on the physicochemical phenomena arranged into abstract (i.e. equipment-independent) functional, structural and behavioural modules. This modularisation framework is used in a methodology to encourage the generation of intensive design strategies. Topological representations are first generated from qualitative knowledge and then mapped into mathematical models. Causal graphs are introduced to allow the designer to identify the relationships between variables relevant to the process. The models are implemented in object-oriented software to quantify the net effect of selected design variables or to quantify equipment requirements. This approach is proposed to increase the flexibility, customisation and reusability of models in order to encourage the implementation and assessment of novel intensified and multifunctional process options.

Keywords: Structure; Behaviour; Phenomena-based modelling; Object-oriented modularisation; Process intensification

1. Introduction

1.1. The unit operations versus the requirements of intensive design

Process intensification (PI) has developed as a revolutionary design philosophy that delivers highly efficient processes involving several combined advantages. However, there are several barriers that prevent the implementation of this philosophy and related novel technologies in industrial processes [1]. The current approach for the implementation of PI is mainly limited to the use of highly efficient devices applying a case-based approach. However, in order to broaden the possibilities for the implementation of the fundamental concepts a deep understanding and systematisation of the design principles implicit in PI developments must be a primary step.

The fundamental thinking underpinning PI involves a multiscale process design [2]. This consists in designing the process (equipment) to perform at the appropriate lengthscale and timescale, according to the ideal requirements at a close-to-molecular level [3,4]. These considerations involve a multiscale challenge as the process design must provide the appropriate environment at the molecular level, while the plant configuration and process equipment need to be designed to operate at the macroscale. This procedure involves then a fundamental multiscale analysis and the understanding of process phenomena and their interrelationships without the spatial constraints of conventional unit operation models and associated equipment. The concept of multiscale process design broadens the possibilities to implement PI because the approach is not limited to the evaluation and use of PI devices. This concept also focuses in the intensification of the process as a whole.

It is important to note a difference between *multiscale process design* and *multiscale modelling*. There are several approaches to rigorous multiscale modelling [5]. These methods model simultaneous phenomena over several orders of magnitude in time and lengthscales using methods such as kinetic Monte Carlo and finite difference code. The multiscale process design focuses to determining the appropriate scale at which a certain physicochemical transformation should be designed as previously discussed.

Based on a performance analysis of the major PI developments, two main design principles for PI can been identified [6]:

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synergistic *integration* of process tasks and coupling of phenomena and targeted *intensification* of transport processes. Taking into account the requirements imposed by these PI principles, traditional unit operation models do not expose the key phenomena relevant to the integration and intensification through a multiscale process design approach. PI has then posed a challenge to the unit operation paradigm in the design and modelling of chemical processes [7].

However, chemical engineering is highly rooted in the concept of unit operations, in such a way that design of chemical processes is still thought of as the problem of connecting unit operations. Optimisation approaches are often limited to determining the optimum interconnection of conventional unit operations under certain constraints. In early stages of conceptual process design most designers think directly in terms of equipment as there is a close relationship between a particular process task and an obvious unit operation [8]. These procedures rely on the existence of equipment or well-defined operations, thereby losing potential opportunities that lie outside this modularisation criterion. Furthermore, adaptation of processes to conventional unit operations involves the acceptance of the inherent inefficiencies of the associated equipment.

Within the simulation context, a library of process unit models has a limited use considering the large and increasing number of potential process units. Novel equipment and process units that do not have an equivalent in the library have to be modelled by using equation-based approaches, which are highly customisable, but require additional effort and cost. As identified by Mangold et al. [9], combined advantages in model flexibility, customisation, reusability, complexity and cost can be gained if model libraries are defined below the level of process units.

1.2. Phenomena-based alternative to the unit operations paradigm

A proper framework for the representation and modelling of processes should then take into account the processes at the molecular scale. This environment should lead to the identification of the main limiting steps and the influences of independent and coupled phenomena. The ultimate goal is the generation (and eventual evaluation) of strategies to overcome the process limitations. Furthermore, the required framework should be flexible enough to exploit the synergy and tackle the complexity derived from multifunctional designs.

The validity of the unit operations paradigm has been questioned by various authors in order to approach innovative designs, and some equipment-independent thinking has been proposed. Siirola [8] presented a task-oriented approach that expands the process alternatives into integrated and more efficient options. Shah et al. [10] suggested that processes should be described in terms of fundamental phenomena and the conditions that are required to allow the process to perform at maximum efficiently. They stated that the definition of “abstract” processes (i.e. independent of equipment and any preconceived unit operations) allows manipulating individual component flows to generate the ideal process conditions. The BRITEST project [11] has developed various methodological tools to capture the process knowledge (i.e. rate processes and phase behaviour) in an equipment-independent way. Batres et al. [12] introduced a modelling approach based on abstract processes implemented as *metamodels* to represent physicochemical behaviours. *Metamodels* are structured to be independent of any equipment and operation context.

Some authors [13–16] have developed alternative phenomena-based methodologies to support process design. However, they do not provide structured and concrete modularisation principles to generate the phenomenological models. Additionally, various authors have developed diverse ideas and concepts regarding a phenomena-based approach as an appropriate way to support the modelling of chemical processes [17–24]. These constitute some of the attempts to overcome the drawbacks and combine the advantages of the modular unit operation-based simulators and equation-based modelling tools. The main contribution is related to the provision of modularisation principles for the generation of phenomena-based building blocks. These approaches have been already implemented in academic prototypes [17,25,26]. However, these are not available in a commercial basis. The phenomena-based concepts have been used to model conventional units, but not to support modelling of innovative designs. Furthermore, none of these modelling approaches has been applied or explored to support the implementation of process intensification principles.

This paper presents a new structure of process design methodologies and process simulation tools in which models are defined in a multilevel unit operation-independent context. *Functional* and *Systems* approaches [27–30] have been employed to structure the framework, in such a way that models are defined in a plant-independent environment. This is a more flexible framework in which the fundamental building blocks have been defined to represent abstract physical elements (i.e. balance volumes) and physicochemical phenomena taking place. The phenomena-based building blocks do not constrain processes to conventional unit operation/equipment boundaries. They can be aggregated or disaggregated according to the best performance and novel designs can be generated.

Phenomena-based building blocks can be translated into the corresponding equations describing them. Then, the different types of terms appearing in the balance equations may be taken as elementary modelling entities. Phenomena-based models can be implemented in the form of a library by means of object-oriented environments in order to facilitate the construction and reuse of models.

2. Phenomena-based modularisation of process models

2.1. Fundamental concepts

This contribution unifies, adapts and uses the concepts developed by the *General Systems Theory* [30] and *Functional Representation* [27–29] in order to structure the framework.

The *Systems* approach develops concepts that can be generically applied to any system, explaining the relationship between the configuration of the systems and their associated performance. The basic concepts are related to the definition of system components based on two main levels (introduced by de Kleer [31]). This approach is used in this contribution to define abstract configurations of chemical processes.

The *structural* level consists of *region elements* and *connection elements*. The former are physical elements defined by permeable, semi-permeable or impermeable boundaries, with accumulation of material and energy as the main attribute. The later are elements that serve to couple region elements, enabling exchange of material and energy. Two region elements should be linked by means of a connection element, establishing flows of material, energy and information.

The *behavioural* level is defined by physicochemical phenomena. These can be defined in an appropriate way by *accumulation*, *generation* and *transport* of material and energy. These phenomena can be manipulated in the form of phenomena-based building blocks, with a related mathematical expression to evaluate their rates defined by the terms in the balance equations as described by Gerstlauer et al. [32]. In this way, a more flexible modelling environment to support the development of novel processes is achieved by means of the aggregation of the terms in the balance equations representing the phenomena-based building blocks.

The *Functional* approach does not explain the detailed performance of individual components, as these are assumed to have a certain structure that allows them to accomplish the function. On the top of the structural and behavioural levels, the Functional approach deals with the representation and analysis of systems at two additional levels: *teleological* and *functional*. Within a design context, the former is related to the design goal assigned to a certain component (i.e. device) and the latter is used to represent the function that the component should perform to achieve the goal. Functional approaches can be used to refine processes in a task-oriented fashion, which allows considering intensification and integration of the whole transformation, not only individual steps.

2.2. Methodology to define and decompose process designs

Fig. 1 shows the relationships between the levels above introduced. Four corresponding levels have been defined for the definition of models of chemical processes:

- *Level 0*. Physicochemical transformation (including business and technical drivers).
- *Level 1*. Process tasks (including but not limited to conventional unit operations and equipment).
- *Level 2*. Interacting *generalised* phases (definition of an abstract process structure).
- *Level 3*. Physicochemical phenomena taking place within or between phases.

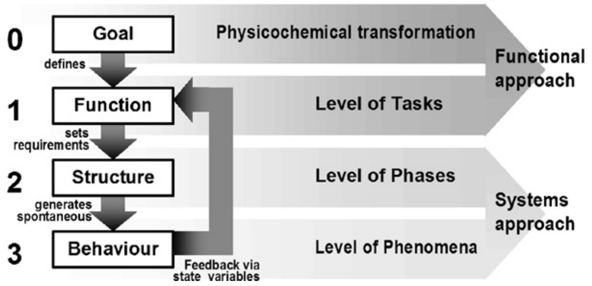

Fig. 1. Consistency and dependence of levels based on systems and functional approaches.

The physicochemical transformation is decomposed at the defined levels and mapped into abstract components. The structural attributes of the components are defined by their topology (interconnection) and the process conditions. The behavioural attributes are defined by the physicochemical phenomena spontaneously occurring within and depending upon the structural attributes. The abstract components are designed to have the desired behaviour by changing their structure to accomplish with the required functionality and achieve the design goals. How the process performs involves finding the relation behaviour = *f*(structure) which means that the behaviour depends only on the structure. A novel interpretation of process design may be then defined as the actions performed to modify the structure in order to produce the desired behaviour that matches the intended function (see Fig. 1).

The modularisation framework defined previously has been applied to guide the construction of process models in a methodology for conceptual process design [33]. This contribution expands this methodology and uses the modularisation criteria to guide the consistent generation, analysis and implementation of qualitative and quantitative models as described in Section 3.

The design methodology proposed in Arizmendi-Sánchez and Sharratt [33] is based on a decomposition of the process at three levels: tasks, phases and phenomena. This procedure begins with the identification and integration of the main *process functions* or *tasks* (i.e. process stages) by looking at the commonalities in functions to be delivered, material involved and process conditions. Main process tasks (including traditional unit operations) are broken down and decomposed into smaller units to define the *process structure*. This is defined by process stages, balance volumes or thermodynamic *phases*. The procedure calls to identify the connections between these structural elements and the influences amongst them. The *process behaviour* is defined by physicochemical *phenomena* consisting of accumulation, generation, convective and diffusive transport, and exchange of material and energy.

3. Phenomena-based modularisation of qualitative and quantitative models

The present contribution uses a hybrid qualitative–quantitative approach as a decision support system. The qualitative modelling component consists of a graphic representation of the process and causal graphs used to support the generation of intensive design strategies. In order to evaluate the proposed strategies under the defined process structure, quantitative modelling is considered when the phenomenological representations are mapped into equations. Consistent mathematical models are hierarchically composed and implemented in object-oriented software as phenomena-based modules.

Table 1
Library of structural and behavioural phenomena-based building blocks

Structural level

- Phases
  - Single phase
    - Vapour, V
    - Liquid inorganic, Li
    - Liquid organic, Lo
    - Solid, S
  - Boundary layers (films)
    - Vapour, V
    - Liquid inorganic, Li
    - Liquid organic, Lo
    - Pores, Po
  - Multiphase (homogeneous)
    - Dispersion, S/L
    - Dispersion, L/S
    - Dispersion, V/L
    - Dispersion, L/V
    - Dispersion, V/S
    - Dispersion, S/V
    - Dispersion, L/L
- Interfaces
  - Physical interface
    - V–Li
    - V–Lo
    - V–S
    - Li–Lo
    - Li–S
    - Lo–S
  - Rigid interface
    - Vessel wall
    - Membrane
    - Filter
    - Fictitious boundaries

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Behavioural level

- Chemical Reaction
- Mass transfer
  - Convection
  - Diffusion
  - Material flow
- Phase change (and phase separation)
  - I. Phase change of single species
    - Evaporation, $L \rightarrow V$
    - Melting, $S \rightarrow L$
    - Sublimation, $S \rightarrow V$
    - Condensation, $V \rightarrow L$
    - Solidification, $L \rightarrow S$
    - Sublimation, $V \rightarrow S$
  - II. Single phase mixing
    - Dissolution, $L_1 + L_2 \rightarrow L$
    - Mixing, $V_1 + V_2 \rightarrow V$
    - Mixing, $S_1 + S_2 \rightarrow S$
  - III. Multiphase mass transfer
    - Dissolution, $L_1 \rightarrow L_2$
    - Reduction of solubility, $L_1 \rightarrow L_2$

Table 1 (*Continued*)

Behavioural level

- Adsorption, $L \rightarrow S$
- Desorption, $S \rightarrow L$
- Adsorption, $V \rightarrow S$
- Desorption, $S \rightarrow V$
- Adsorption, $V \rightarrow L$
- Stripping, $L \rightarrow V$

- IV. Multiphase dispersion
  - Dispersion, $L_1 + L_2 \rightarrow L_2/L_1$
  - Separation, $L_2/L_1 \rightarrow L_1 + L_2$
  - Dispersion, $L + S \rightarrow S/L$
  - Settling, $S/L \rightarrow L + S$
  - Dissolution, $L + S \rightarrow L$
  - Precipitation, $L \rightarrow L + S$
  - Dispersion, $L + V \rightarrow V/L$
  - Separation, $L/V \rightarrow V + L$
  - Dispersion, $V + L \rightarrow L/V$
  - Disengagement, $V/L \rightarrow L + V$
  - Dispersion, $V + S \rightarrow S/V$
  - Separation, $S/V \rightarrow V + S$
  - Wetting, $S + L \rightarrow L/S$
  - Drying, $L/S \rightarrow S + L$

- Energy phenomena
  - Convection
  - Conduction
  - Radiation
  - Generation/source
    - Heat of reaction
    - Heat of solution
    - Mechanical
    - Electrical
    - Shear
    - Ultrasound
    - Microwaves
- Change conditions
  - Temperature increase
  - Temperature decrease
  - Pressure increase
  - Pressure decrease
  - Velocity increase
  - Velocity decrease
- Mechanical operations
  - Attrition
  - Agglomeration

3.1. *Library of phenomena and graphical representation*

In order to define an equipment-independent structure of chemical processes, these can be considered as an aggregation of interacting thermodynamic phases as proposed by Perkins et al. [34]. The advantage of using thermodynamic phases as fundamental building blocks for the development of novel multiphase reactors has been recognised by Mehta and Kokossis [35].

For the purposes of steady-state representation, this contribution uses thermodynamic phases as elementary modelling units to define process models at the structural level. Because region elements are defined as any kind of balance volume with accumulation of material/energy, the term “level of phases” (see Fig. 1) is applied in a broader sense, not only referring to thermodynamic phases. In this way it is possible to define regions or volumes with different conditions such as boundary layers under the same concepts and topology.

For the behavioural level, the most relevant phenomena that will enable the construction of the major part of process models have been identified and classified as shown in Table 1. Based on the library of phenomena shown, a graphical topology has been devised. This phenomenological description of the process is based on the phenomena-based process representation (PBPR) presented in Arizmendi-Sánchez et al. [36]. This topology is analogous to the one developed by Drengstig et al. [21] and Wall et al. [37], but aims to provide a more intuitive representation within the context of the structuring fundamentals here presented. PBPR is a *state-based* approach composed by nodes representing a transformation or phenomenon, and arcs defining states or inventory/accumulation models. It may be interpreted as a representation of the process tasks that the process design must fulfil (i.e. the process requirements).

This representation aims to assist in the identification of main phenomena involved in the process, the location where these take place, their sequence and influences. It is used to provide a clearer vision of the process at the molecular level and to identify the fundamental requirements that provide the ideal conditions. This type of representation also provides a shared language between chemists and engineers involved in the process development [11,37].

3.2. Qualitative modelling with causal graphs

As expressed by Sharratt [38], in the early stages of process development, and in particular for complex processes such as those found in pharmaceuticals and specialty chemicals, detailed mathematical modelling is not feasible. The use of qualitative models has been established as a mechanism to deliver many of the useful conclusions of a mathematical modelling approach, but much earlier in design.

Approaches for the qualitative modelling of processes based on influences and interactions of phenomena are derived from the qualitative process theory (QPT) of Forbus [39]. Qualitative modeling has the distinctive feature of using causal representations, revealing the effects of variables on other variables. Causal graphs are useful to qualitatively model the behaviour of a system as it is possible to identify all the interrelationships between elements and establish dependencies. Causal graphs can be defined at various levels in order to analyse the influences the between physical or mathematical components.

State-based representations such as the PBPR can be used to perform a qualitative modelling of the process in the way of a cause-effect analysis when they are represented as signed directed graphs [40]. Because PBPR has been built on the balance equations it can be used as a phenomenological description to support the generation of model equations. One can then construct a “variable-based causal graph” (VBCG), corresponding to the “causal ordering” of Iwasaki and Simon [41]. These are signed directed graphs consisting of all the process variables as the nodes and arcs representing the direct or indirect relationships between a pair. VBCGs are used to analyse the relationships and influences between variables to devise intensive design strategies.

Qualitative models (in the form of causal graphs) are solved by determining the effect of process influences on variables and propagating these effects through the causal links to other variables ultimately representing the key process outcomes (e.g. yield, efficiency) [42]. By manipulating the exogenous variables representing driving forces one can analyse the effect on rate phenomena defined by dependent variables. Coupled phenomena are in general represented by interdependent variables (variables dependent on each other or calculated at the same time).

Causal graphs provide improved insights into the process performance, which makes them appropriate for the purposes of intensive design. The qualitative modelling approach makes more evident the degrees of freedom, making easier the identification of potential design and operating strategies to be evaluated with quantitative approaches.

3.3. Modularisation criteria to generate phenomena-based mathematical models

In order to evaluate the design options, quantitative modelling is considered when the phenomenological representations are mapped into equations and implemented in computer-aided modelling environments. Quantitative modelling is used to quantify the effect of the proposed process configurations and conditions or to quantify equipment requirements by means of sensitivity analyses of the variables with significant influence.

Having defined the equations describing the process, appropriate modularisation criteria are needed to produce the suitable phenomena-based models. The modules can be defined in function of structural components (such as process tasks, abstract units, phases, balance volumes, physical regions, etc.) and also behavioural elements (i.e. physicochemical phenomena). Equations and variables describing accumulation, reaction and transfer *phenomena* are grouped as primitive models. These are then aggregated to create the composite models defining *phases* (i.e. the physical volumes/regions in which the phenomena take place). Further aggregation creates composite models at higher levels defining process *tasks* (e.g. process stages or devices) and finally the whole processes (i.e. the process flowsheets). The causal relationships between modules are defined via the port variables. This reduces the complexity of the variable-based causal graph and makes easier the cause and effect analyses.

Multilevel models representing functional, structural and behavioural building blocks are consistently supported by equation-based software built on object-oriented architectures. This contribution uses aspen custom modeler (ACM) to implement the models and perform the numerical simulation of the process.

The use of these more fundamental building blocks provides a flexible environment, enabling model reuse and fast model construction when assessing different configurations. The multilevel feature of the framework provides an improved flexibility to model novel processing options such as integrated operations that cannot be modelled with traditional models included in unit operation-based libraries. Multifunctional reactors can be modelled by aggregating the appropriate building blocks in the form of convective, diffusive and reactive elements at the level of phenomena, i.e. by adding/removing terms in the balance equations.

4. Modelling case: competing reactions in a well-mixed system

Consider a reaction scheme with two competing reactions in liquid phase:

Reaction 1 $A + B \rightarrow C$ (exothermic)

Reaction 2 $C + B \rightarrow D$ (endothermic)

where C is the desired product and the generation of D should be minimised as it is a side product that reduces the overall yield. This is a typical scheme in processes with reactions involving consecutive additions/substitutions of functional groups (e.g. nitrations, acetylations, hydrogenations, etc.). Consider that after applying the methodology described by Arizmendi-Sánchez and Sharratt [33] this is the main process task. Consider also that due to technical and business constraints, the best overall process should be carried out in a well-mixed regime, so the system is then considered to be limited only by chemical rates. Additionally consider that the system requires the removal of generated heat by means of a conventional cooling fluid (i.e. water).

It should be noted that under the design approach, the process should be initially mapped into the appropriate tasks and not necessarily conventional unit operations (such as the well-mixed system in the example). In this case this model is used only for demonstration purposes, and the operation should be still considered as an abstract task with certain regime characteristics (generic well-mixed system) which has been defined as the most appropriate way to perform the physicochemical transformations. A more complex example also handled under equipment-independent considerations is described by Arizmendi-Sánchez and Sharratt [6,33] for the Paracetamol process.

4.1. Phenomena-based process representation

Fig. 2 shows the phenomena-based topological representation of the well-mixed reactor with a coupled heat transfer unit. The structural elements and their interconnection are defined first and represented as blank spaces. Subsequently, the phenomena occurring within and between structural elements are represented, identifying the potential interrelationships and sequence. Model assumptions are taken into account. In this example a well-mixed model is used, so convective/diffusive transport processes are not represented.

Based on a hierarchy of models, these are consistently defined at the three levels explored in this contribution (see Fig. 4). “Reactor” corresponds to the *task* or function to be achieved by means of the component structure and resultant behaviour. This task is refined into two *phases* or region elements i.e. reacting mixture (vessel) and cooling media (jacket), linked through a connection element (i.e. vessel wall). Reactor, vessel and jacket should be physically understood as generic spatial components, in such a way that any equipment option can be considered. The behaviour is defined by the *phenomena* occurring inside the structural elements as a result of the structural configuration (i.e. interconnection and process conditions). The phenomena in this system consist of reactions (generation/consumption of material and energy), flow of fluids through the system and heat transfer.

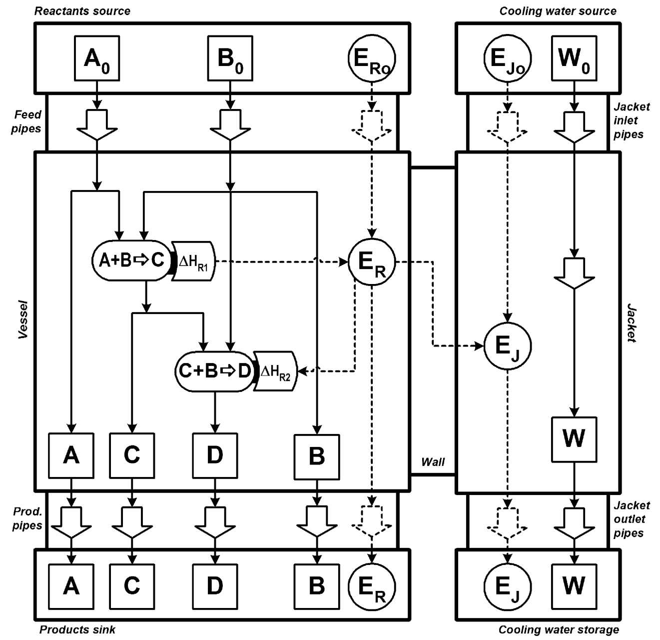


Fig. 2. Phenomena-based process representation of the well-mixed cooled reactor with competing reactions.

4.2. Equation mapping from phenomenological description

The phenomenological description (topologically represented in Fig. 2) can be seen as a graphical representation of the material and energy balance, so it can be used to generate the model equations as follows:

Generic balance equation real system:

$$\text{accumulation} = \text{diffusive transport} + \text{convective transport} + \text{transport through boundaries} + \text{reaction} \quad (1)$$

Generic balance equation well-mixed system:

$$\text{accumulation} = \text{transport through boundaries} + \text{reaction} \quad (2)$$

$$\text{accumulation} = (\text{flow in} - \text{flow out}) + \text{reaction} \quad (3)$$

Material balances in “Vessel” volume:

$$A_{\text{vessel}} = (A_{\text{in}} - A_{\text{out}}) - A_{\text{reaction 1}} \quad (4)$$

$$B_{\text{vessel}} = (B_{\text{in}} - B_{\text{out}}) - (B_{\text{reaction 1}} + B_{\text{reaction 2}}) \quad (5)$$

$$C_{\mathrm{vessel}} = -C_{\mathrm{out}} + (C_{\mathrm{reaction\ 1}} - C_{\mathrm{reaction\ 2}}) \tag{6}$$

$$D_{\mathrm{vessel}} = -D_{\mathrm{out}} + D_{\mathrm{reaction\ 2}} \tag{7}$$

Material balances in “Jacket” volume:

$$W_{\mathrm{jacket}} = W_{\mathrm{in}} - W_{\mathrm{out}} \tag{8}$$

Energy balance in “Vessel” volume:

$$E_{\mathrm{vessel}} = (E_{\mathrm{vessel\text{-}in}} - E_{\mathrm{vessel\text{-}out}}) - E_{\mathrm{reaction\ 1}} - E_{\mathrm{reaction\ 2}} - Q \tag{9}$$

Energy balance in “Jacket” volume:

$$E_{\mathrm{jacket}} = E_{\mathrm{jacket\text{-}in}} - E_{\mathrm{jacket\text{-}out}} + Q \tag{10}$$

The equations are further refined by means of the corresponding constitutive equations and in terms of the appropriate variables. At this point, a specific technology option should be selected in order to define specific geometry constrains required in the refinement of equations.

It is important to note that PI designs approach the ideal models, in such a way that the assumptions are more valid than for conventional equipment. Real PI equipment and design strategies are used to make assumptions valid as they represent an ideal performance. For this case, one could think of a jacketed stirred vessel with a recycle loop containing a jet or static mixer (jet-loop or buss-loop reactor) to approach the well-mixed system. This is a plant configuration that matches the process requirements as initially identified. We can use this technology option in order to deal with the definition of the geometry of the system, which is required for the rigorous quantitative modelling. Additionally consider that the output flow is proportionally controlled using the level in the tank, and that the jacket operates at constant level.

The set of equations is shown below. The variables involved are described in Table 2, including the values that will be used later in the ACM simulation.

Material balances in Vessel:

$$\frac{\mathrm{d}M_{\mathrm{A}}}{\mathrm{d}t} = F_0 C_{\mathrm{A0}} - F C_{\mathrm{A}} - r_1 V \tag{11}$$

$$\frac{\mathrm{d}M_{\mathrm{B}}}{\mathrm{d}t} = F_0 C_{\mathrm{B0}} - F C_{\mathrm{B}} - r_1 V - r_2 V \tag{12}$$

$$\frac{\mathrm{d}M_{\mathrm{C}}}{\mathrm{d}t} = -F C_{\mathrm{C}} + r_1 V - r_2 V \tag{13}$$

$$\frac{\mathrm{d}M_{\mathrm{D}}}{\mathrm{d}t} = -F C_{\mathrm{D}} + r_2 V \tag{14}$$

The total material balance can be expressed as

$$\frac{\mathrm{d}V}{\mathrm{d}t} = F_0 - F \tag{15}$$

Constitutive equations:

$$M_{\mathrm{A}} = C_{\mathrm{A}} V \tag{16}$$

$$M_{\mathrm{B}} = C_{\mathrm{B}} V \tag{17}$$

$$M_{\mathrm{C}} = C_{\mathrm{C}} V \tag{18}$$

Table 2
Variables involved in the model

Variable	Description	Value
C_{A0} (kmol/m^3)	Concentration A inlet	8
C_{A} (kmol/m^3)	Concentration A outlet	–
C_{B0} (kmol/m^3)	Concentration B inlet	5
C_{B} (kmol/m^3)	Concentration B outlet	–
C_{C0} (kmol/m^3)	Concentration C inlet	0
C_{C} (kmol/m^3)	Concentration C outlet	–
C_{D0} (kmol/m^3)	Concentration D inlet	0
C_{D} (kmol/m^3)	Concentration D outlet	–
r_1 (kmol/m^3 h)	Reaction rate 1	–
r_2 (kmol/m^3 h)	Reaction rate 2	–
F_0 (m^3/h)	Vessel inlet flow	11
F (m^3/h)	Vessel outlet flow	–
F_{W0} (m^3/h)	Cooling water inlet flow	40
F_{W} (m^3/h)	Cooling water outlet flow	–
T_0 (°C)	Vessel inlet temperature	150
T (°C)	Vessel outlet temperature	–
T_{W0} (°C)	Cooling water inlet temperature	25
T_{W} (°C)	Cooling water outlet temperature	–
Q (kJ/h)	Heat duty	–
V (m^3)	Vessel volume	–
V_{J} (m^3)	Jacket volume	1.5
C_{v} (m^2/h)	Valve coefficient	5
d (m)	Vessel diameter	2
U (kJ/m^2 h K)	Heat transfer coefficient	2,000
A_{J} (m^2)	Jacket area for heat transfer	–
h_{min} (m)	Min. liquid level in vessel	1
h (m)	Liquid level in vessel	–
ρ (kg/m^3)	Mixture density	800
ρ_{W} (kg/m^3)	Water density	1,000
C_p (kJ/kg K)	Mixture heat capacity	3
$C_{p\mathrm{W}}$ (kJ/kg K)	Water heat capacity	4.186
ΔH_{R1} (kJ/kmol)	Heat of reaction 1	−100,000
ΔH_{R2} (kJ/kmol)	Heat of reaction 2	50,000
E_{act1} (kJ/kmol)	Activation energy reaction 1	90,000
E_{act2} (kJ/kmol)	Activation energy reaction 2	100,000
k_{01} ($\times 10^{12}$ m^3/kmol h)	Pre-exp factor reaction 1	2.3
k_{02} ($\times 10^{12}$ m^3/kmol h)	Pre-exp factor reaction 2	1.0

$$M_{\mathrm{D}} = C_{\mathrm{D}} V \tag{19}$$

$$r_1 = k_{01} \exp\left(\frac{-E_{\mathrm{act\ 1}}}{RT}\right) C_{\mathrm{A}} C_{\mathrm{B}} \tag{20}$$

$$r_2 = k_{02} \exp\left(\frac{-E_{\mathrm{act\ 2}}}{RT}\right) C_{\mathrm{B}} C_{\mathrm{C}} \tag{21}$$

$$V = \frac{\pi}{4} d^2 h \tag{22}$$

$$F = C_{\mathrm{v}}(h - h_{\mathrm{min}}) \quad \text{reactor level control} \tag{23}$$

Material balances in Jacket:

$$\frac{\mathrm{d}V_{\mathrm{J}}}{\mathrm{d}t} = F_{\mathrm{W0}} - F_{\mathrm{W}} \tag{24}$$

Energy balance in Vessel:

$$\frac{\mathrm{d}E_{\mathrm{R}}}{\mathrm{d}t} = F_0 \rho_0 C_{p_0} T_0 - F \rho C_p T - r_1 V \Delta H_{R1} - r_2 V \Delta H_{R2} - Q \tag{25}$$

Constitutive equations:

$$E_{\mathrm{R}} = V\rho C_p T \tag{26}$$

Energy balance in Jacket:

$$\frac{\mathrm{d}E_{\mathrm{J}}}{\mathrm{d}t} = F_{\mathrm{W0}}\rho_{\mathrm{W0}}C_{p\mathrm{W0}}T_{\mathrm{W0}} - F_{\mathrm{W}}\rho_{\mathrm{W}}C_{p\mathrm{W}}T_{\mathrm{W}} + Q \tag{27}$$

Constitutive equations:

$$E_{\mathrm{J}} = V_{\mathrm{J}}\rho_{\mathrm{W}}C_{p\mathrm{W}}T_{\mathrm{W}} \tag{28}$$

Coupling of systems through heat transfer:

$$Q = UA_{\mathrm{J}}(T - T_{\mathrm{W}}) \tag{29}$$

Constitutive equations:

$$A_{\mathrm{J}} = \frac{\pi}{4}d^2 + \pi dh \tag{30}$$

4.3. Variable-based causal graph

The variable-based causal graph (VBCG) for the system is depicted in Fig. 3. All the relationships between the variables and their relative positive or negative influences (i.e. direct or indirect relationships) have been identified. It is possible to identify the various types of variables in order to analyse potential scenarios by manipulating the exogenous (i.e. independent or input) variables.

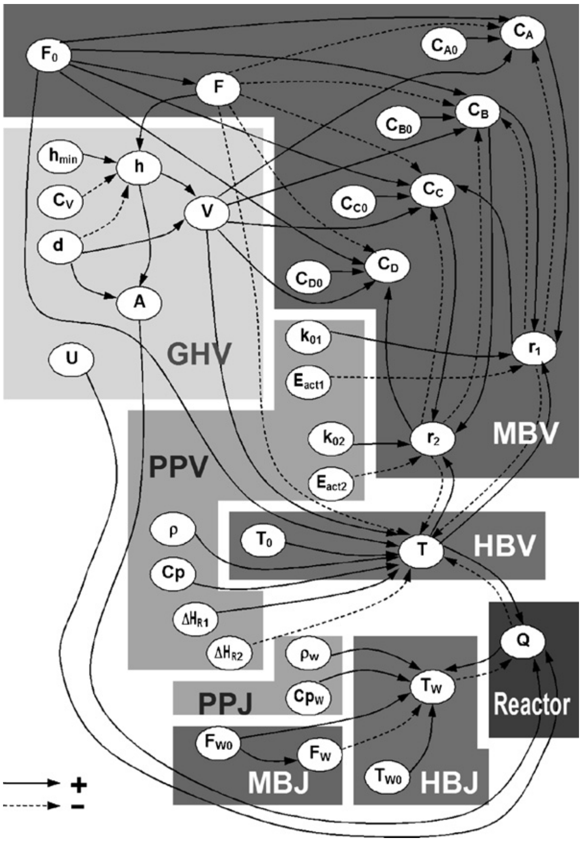


Fig. 3. Variable-based causal graph for the reactor model.

The objective of this approach is to perform a qualitative modelling of the system that should provide with increased insights into which variables (i.e. driving forces) should be manipulated to have the desired effects (e.g. increase rates of limiting phenomena). For this case one should devise design strategies to maximise the production of C. For example, by means of the VBCG one can analyse the effect of the temperature on the concentrations of both products (through the rate of both reactions). Applying conventional heuristic knowledge, one may think of reducing the temperature to encourage the desired exothermic reaction and suppress the endothermic side-reaction. However, it is clear from the VBCG that the temperature has a direct effect in the kinetic constants of both reactions.

4.4. Phenomena-based modularisation for the computer implementation

Competing effects unsolved by qualitative modelling should be resolved through quantitative modelling. Apart from quantifying the net effect of selected design variables, solution of numerical models may enable the calculation of equipment requirements or appropriate operative ranges.

A consistent phenomena-based modularisation of models will enable coherence in the method and will provide modelling advantages such as increased flexibility, customisation and reusability of models. In the VBCG shown in Fig. 3, some variables have been grouped by shaded areas as they are related to certain potential models (acronyms defined in Fig. 5). The variables and equations involved in this example can be initially grouped in modules defined by material and energy balances as a first approach to generate the phenomena-based building blocks. This method should be particularly useful to tackle the complexity of larger and more rigorous cases. The primitive models are defined as the blocks shown because this example is not so complex to perform further refinement through pure phenomena-based models (i.e. reaction, transport and accumulation models). In this case we identified a further opportunity to group in a module variables related to the calculation of physical properties and other module regarding system geometry and hydraulic issues. This is considered only in order to expand the demonstration of the modularisation at the behavioural level. However these variables/equations could be consistently included in the corresponding phenomenological model (generally as exogenous variables).

These models are arranged in the hierarchy shown in Fig. 4. As shown in the diagram, the composite models can be consistently defined at the three levels explored in this contribution. This hierarchy of models is also consistent with the process structure represented in Fig. 2. Primitive models are defined at the behavioural level and aggregated to produce composite models at the structural level. At the higher functional level, the composite model "Reactor" is generated from the aggregation of the corresponding subcomposite models "Vessel" and "Jacket".

The models are implemented in ACM based on the model structure depicted in Fig. 5. This diagram can be understood as a causal graph at a higher level, in which the relationships

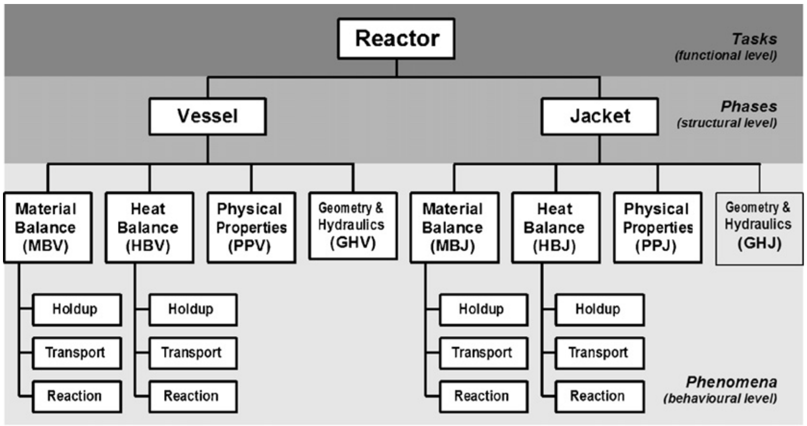
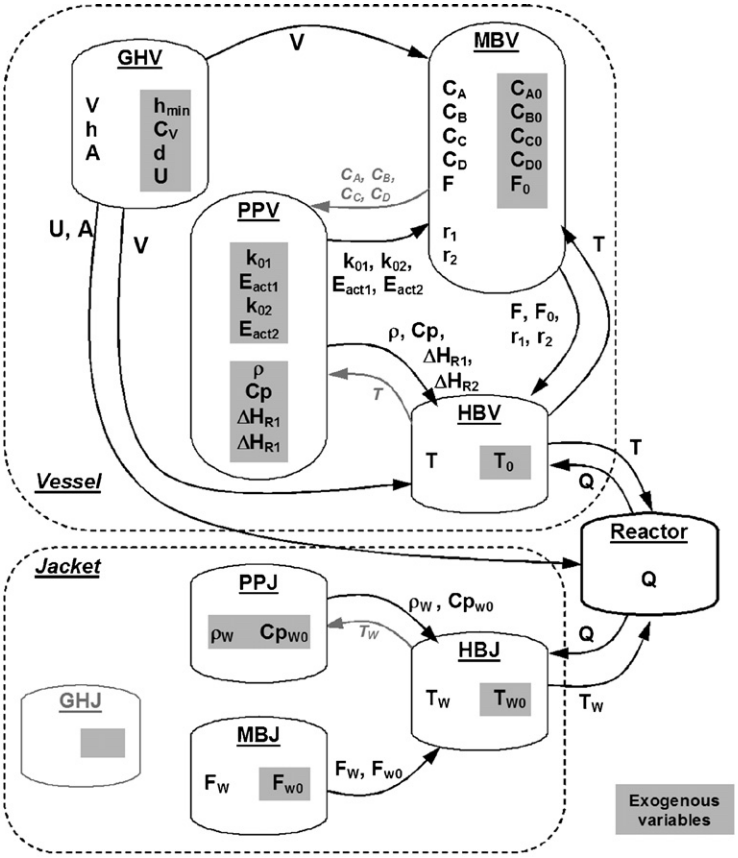


Fig. 4. Hierarchy of models for the reactor model.



Primitive models	Composite Models
MBV – Mass balance model of vessel	Vessel – Composite model containing [MBV], [HBV], [PPV] and [GHV] models
HBV – Heat balance model of vessel	
PPV – Physical properties model of vessel	
GHV – Geometry and Hydraulics model of vessel	Jacket – Composite model containing [MBJ], [HBJ], [PPJ] and [GHJ] models
MBJ – Mass balance model of jacket	
HBJ – Heat balance model of jacket	
PPJ – Physical properties model of jacket	Reactor – Composite model containing [Vessel] and [Jacket] models
GHJ – Geometry and Hydraulics model of jacket	

Fig. 5. Modules and port variables for the ACM implementation of the reactor model.

and influences between modules are defined through the port variables (shared information).

4.5. Quantitative modelling in Aspen Custom Modeler

The model was implemented as described in the preceding section using ACM, with the process conditions defined in Table 2. One could perform innumerable quantitative analysis but in the interest of space limitations we will demonstrate the usefulness with a few issues.

Qualitative modelling has the weakness of being unable to resolve competing effects and hence produces multiple solutions [18]. Quantitative modelling is used to estimate the system behaviour under the prevailing process conditions and system topology. For this example it has been identified that the process can be designed to have the desired behaviour (i.e. maximise the rate of production of C) by manipulating the reactor temperature. A detailed study on the temperature effects was applied by performing a sensitivity analysis $\delta C_i/\delta T$. The objective was to analyse the net effect of a temperature increase in the composition of the reacting mixture, particularly the concentration of the product C. The temperature of the reactor T was set as fixed variable and the inlet process temperature T_0 (or alternatively the cooling water inlet temperature T_{W0}) as free variable.

This sensitivity analysis was performed for various values of the ratio of initial reactants concentration C_{A0}/C_{B0} (i.e. 8/3, 8/5, 8/7, 8/8, 7/8, 5/8). The net effect of the temperature over the product final concentration is shown in Fig. 6. It is clear that the initial concentration of B should be limited as it encourages the generation of the by-product D (effect that can be previously identified clearly in the VBCG). For the extreme case in which an excess of B ($C_{A0}/C_{B0} = 5/8$) produces a high amount of D, the increase in the reactor temperature initially causes a higher rate of the reaction 1, encouraging the production of C. However, after a peak in C_C is reached (at 120 °C) an increase in the reaction temperature decreases the production of the desired product C and encourages the rate of the side reaction. This effect is reduced as the relative initial concentration of B is decreased, however this pattern is still noticeable at the ratio $C_{A0}/C_{B0} = 8/5$.

In this way, the net effect identified by means of the causal relationships is quantitatively evaluated. As expressed before, based on conventional heuristic rules, one could think of applying intensive heat removal strategies to maintain the reaction temperature low, in such a way that the endothermic side reaction is discouraged. However, in this case the side reaction is intrinsically slow, and the temperature has a higher effect on the desired reaction than on the side reaction. The opposite design strategies should be then applied, i.e. the operation at high temperatures, limited only by potential safety and product degradation issues. This is true only at temperatures below 120 °C, having an opposite effect in the upper range. At temperatures higher than 120 °C, an appropriate (intensive) heat removal should be considered in order to guarantee the low production of D.

Based on a heuristic reaction engineering approach, one may think early of using an excess of A to reduce the side reaction that consumes the other reactant B. In this way, the process option using $C_{A0}/C_{B0} = 8/3$ has the highest selectivity, which represents a reduction of the impurities and potential waste. This also reduces the separation duty to isolate the by-product. It also has

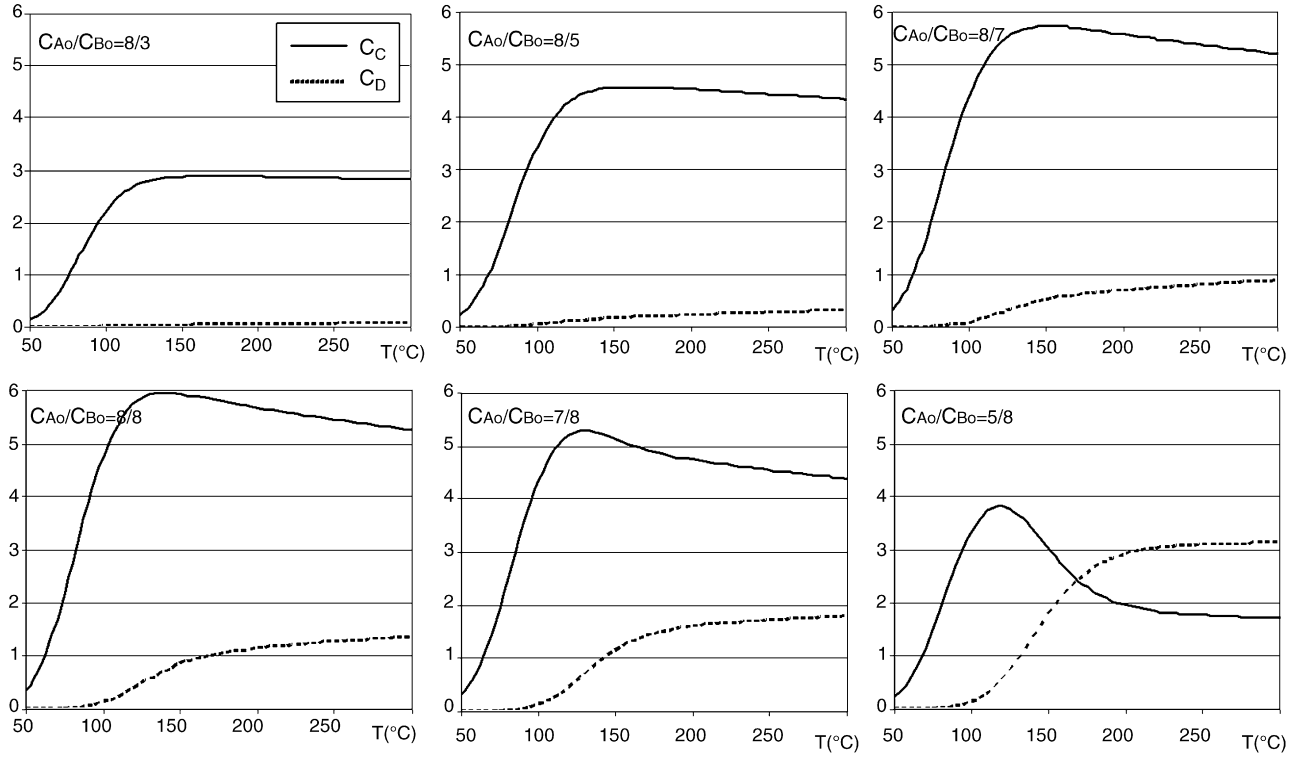


Fig. 6. Concentration of products C and D as function of reactor temperature for various ratios of initial reactants concentration (C_{A0}/C_{B0}).

the advantage of being potentially carried out adiabatically as mentioned before. However this option requires an increased recycle of the reactants because the conversion is low. On the other hand, the results here presented indicate that the option that uses a stoichiometric ratio of reactants has a higher conversion. However, for this case the process conditions (i.e. temperature) should be accurately controlled to achieve the optimum performance (i.e. maximum concentration of C). This involves the operation at isothermal conditions provided by e.g. intensive heat removal. These findings should be taken into account to select the equipment that provides these requirements. The ultimate criteria to select the process option should consider the business constrains (e.g. costs of both options).

The computer model can be used to quantify the net effect of other selected design variables or to quantify equipment requirements. For example, for the case in which isothermal operation is required, a sensitivity analysis of the temperature and heat transfer area can be performed with the same model. This analysis provides values of the range of heat transfer areas required to maintain the temperature over the required value. Then these data should be matched with the available commercial equipment database. Similar analyses could be performed, for example, to define requirements of interfacial mass transfer area in heterogeneous systems and the specific operative variables that provide the required interfacial area.

The typical example here presented has been used to demonstrate the usefulness of the approach by making evident degrees of freedom and their manipulation for the generation of intensive design strategies. Even when some of the solutions may appear trivial to reaction engineering, the example demonstrates these capabilities and the strengths of the approach. Additional insights and findings are made evident in contrast with the use of conventional methods and generic heuristic rules. Equipment requirements under particular conditions (e.g. being adiabatic or isothermal) are also made more evident.

Furthermore, the models have been built and stored in a flexible and customisable environment, in such a way that similar models (including conventional unit processes) can be built easier, faster and cheaper from an expanding library of typical phenomena-based building blocks. Because the model libraries are built under the same modularisation criteria, new mathematical models can be used consistently with the proposed methodologies for conceptual process design.

5. Conclusions

Innovative design philosophies such as PI have introduced a paradigm change in which chemical processes are designed and operated. Existing PI developments have demonstrated that combined advantages are gained when the unit processes, conditions, geometries and related equipment are defined and dimensioned only after the ideal process configuration that delivers the required transformation has been identified. This involves the manipulation of the degrees of freedom in a resilient design and modelling environment which is not constrained by any predefined geometries, existing unit operation models and related equipment.

An increased flexibility to produce models integrated at various levels from the molecular requirements to complex integrated operations can be achieved by defining the building blocks at lower levels. The use of modelling to support intensive design means to devise strategies for decomposing the physicochemical transformation into smaller independent functions and define control actions that achieve and maintain those functional structures.

A phenomena-based framework for the refinement of designs and modelling of processes has been presented. *Functional* and *Systems* approaches have been explored and unified in order to provide more natural and context independent modularisation criteria. This contribution presented specific and simple modularisation principles to define these abstract (i.e. equipment-independent) models. Furthermore, a concrete library of typical phenomena-based building blocks has been provided to assist the representation and qualitative modelling of chemical processes. These building blocks have been created on the basis of the balance equations, which enables the consistent generation of mathematical models from phenomenological descriptions.

The multilevel representations (matching the mental representations) can be used to perform qualitative modelling which may give the first insights into the process performance. Because the designer constructs the process models and representations himself with a focus in the pure molecular processes, the models are no longer black boxes. This model-based reasoning exploits the use of causal relationships between process variables associated with driving forces and physicochemical phenomena. These representations are then used to support the generation of intensive design strategies. Findings from qualitative models also serve to guide quantitative modelling in order to evaluate the devised options. Sensitivity analyses are applied to identify variables with significant influence or to define required ranges of variables associated with equipment features.

Multilevel models representing functional, structural and behavioural building blocks can be consistently implemented in equation-based software built on object-oriented architectures. Phenomena-based building blocks can be implemented in the form of a library in order to facilitate the construction and reuse of models. Combined advantages are then gained in model flexibility, customisation, reusability, complexity and cost. The use of these building blocks at a lower level of aggregation should enable construction and customisation of a large number of processes. In this way, evaluation of novel unconventional but highly efficient processes may be performed with an acceptable level of complexity and cost. Equally, these models are still suitable for the design of traditional plants involving conventional operations.

This is a more flexible equipment-independent approach to the required multiscale modelling that enables the capture of non-trivial features and exposes key phenomena. The potential more efficient options are increased as the process is not constrained early to unit operations, revealing features of intensification and making explicit the associated degrees of freedom. This approach provides increased insights into the processes being modelled and an appreciation of the cause and effect, expanding the heuristic rules from the early development of PI. It encourages the implementation of PI principles regarding both the enhancement and the coupling of phenomena via the generation of alternatives derived from model-based reasoning.

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