

## **Hybrid modelling methodology to implement chemical process models as phenomena-based modules**

Jorge A. Arizmendi-Sánchez, Paul N. Sharratt

*School of Chemical Engineering and Analytical Science, The University of Manchester,  
P.O. Box 88 Manchester M60 1QD, United Kingdom,  
J.Arizmendi-Sanchez@postgrad.manchester.ac.uk*

### **Abstract**

This paper presents a hybrid framework to represent and analyse qualitative knowledge about chemical processes to encourage the generation of intensive design strategies. The methodology includes the mapping of qualitative models into mathematical models to quantify the effect of the proposed process configurations and conditions or to quantify equipment requirements. Models are based on the physicochemical phenomena arranged into abstract (i.e. equipment-independent) functional, structural and behavioural modules. These are consistently implemented using the object-oriented features of Aspen Custom Modeler. This approach is proposed to increase the flexibility, customisation and reusability of models to encourage the implementation and assessment of novel intensified and multifunctional options. The application of the methodology is illustrated with an aromatic nitration case study.

**Keywords:** physicochemical phenomena, qualitative modelling, cause-effect analysis, phenomena-based modularisation.

### **1. Introduction**

Innovative design philosophies such as Process Intensification (PI) have introduced a paradigm change in which chemical processes are designed and

operated. It has been demonstrated that combined advantages in efficiency, size, costs, and environmental and safety issues are gained when the unit processes, conditions, geometries and related equipment are defined and dimensioned only after identifying the ideal process configuration to deliver the required transformation. 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. It has been identified that alternative methods and tools are required to encourage and support the generation of intensive processes [1]. Process design is still thought of as the problem of connecting unit operations, thereby missing potentially more-efficient designs such as multifunctional units. Also, conventional process simulators have limited model libraries which cannot be customised in an easy way for the modelling of novel unit processes.

An increased flexibility to produce models integrated at various levels from the molecular requirements to complex integrated operations can be achieved by defining the modules at lower levels. Based on PI principles, processes should be described in terms of fundamental phenomena and the conditions that are required to allow the process to perform at maximum efficiency [2]. The need to define models below the unit operations has been already explored as an appropriate way to model chemical processes, giving advantages such as flexibility and reusability [3-6]. This thinking has been already implemented in academic prototypes [7-9]. However, these are not available in a commercial basis. Furthermore none of these approaches and tools has been linked to the generation of intensified processes and integrated within a design framework.

## 2. Phenomena-based framework

This paper presents a modelling framework in which process models are refined in a multilevel unit-operation-independent context using *Functional* and *Systems* approaches.

### 2.1. Modularisation structure

The physicochemical transformation is decomposed into abstract (i.e. equipment-independent) models [10] based on the following level hierarchy.

1. **Functional level.** Definition of the main process TASKS.
2. **Structural level.** Models defined by abstract physical elements (i.e. balance volumes) generically called PHASES. The structural attributes of the abstract components are defined by their topology (interconnection) and the process conditions.
3. **Behavioural level.** The behavioural models are defined by the physicochemical PHENOMENA spontaneously occurring within the abstract components and depending upon the structural attributes. The different types

of terms appearing in the balance equations are taken as elementary modelling entities.

The abstract components (which are independent of any equipment and operation context) are designed to have the desired behaviour via changes in their structure to accomplish with the required functionality. These abstract components implemented as *metamodels* can be hierarchically composed. Models at lower levels are associated with equation models and can be consistently implemented in object oriented environments [6].

## 2.2. Qualitative modelling

The qualitative modelling component of this framework consists of a state-based topological representation and causal graphs. A concrete library of typical phenomena-based building blocks has been provided to assist the representation and qualitative modelling of chemical processes [1]. 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 equations are translated into variable-based causal graphs (VBCG) representing the dependences between variables. These are signed directed graphs consisting in all the process variables as the nodes and arcs representing the direct or indirect relationships between a pair. VBCG's are solved by determining the effect of process influences on variables and propagating these effects through the causal links to other variables. These qualitative models are used to generate potential design and operating strategies to be evaluated.

## 2.3. Quantitative modelling

Qualitative modelling has the weakness of being unable to resolve competing effects and hence produces multiple solutions. Quantitative modelling is used to resolve ambiguous effects by estimating the system behaviour under the prevailing process conditions and system topology. The equations are grouped in functional, structural and behavioural building blocks and consistently implemented using the object-oriented features of Aspen Custom Modeler (ACM). These models are 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.

## 3. Aromatic nitration case study

Aromatic nitrations involve a very fast reaction with yield and selectivity limited by mass transfer rates. The mixing efficiency has a direct effect in providing a fine phase dispersion to increase the interfacial area. Considering the mononitrated aromatic (NA) as the product of interest, there are some side-reactions in series (di- and tri-nitration) and in parallel (oxidations to

nitrophenols). The reactions are shown in figure 1. The main steps (m) for the production of NA involve the production of the nitronium ion  $\text{NO}_2^+$  by means of the dissociation of  $\text{HNO}_3$  (N) with  $\text{H}_2\text{SO}_4$  (S). The nitration takes place in the acid phase, requiring the diffusion of the aromatic (A) through the interface.

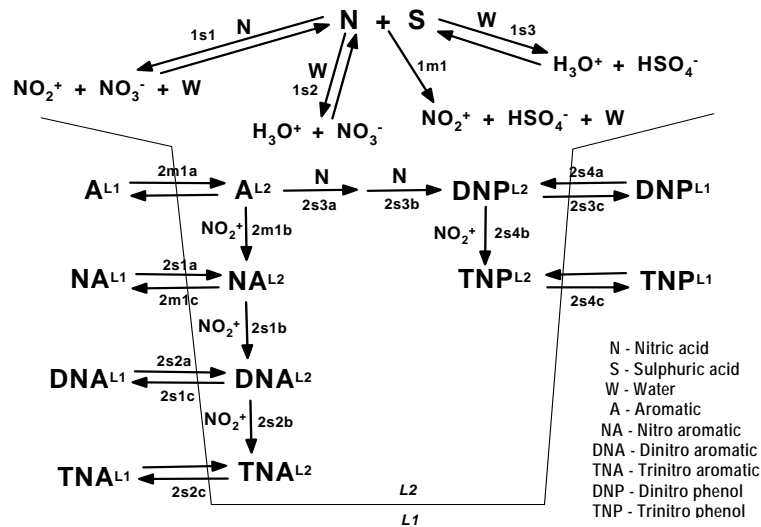


Figure 1. Reaction map for the main and side reactions in the nitration of aromatics [11]

### 3.1. Qualitative modelling: conceptual design

By means of a Driving Force Analysis [10, 12] it is possible to identify early in design the main tasks and conditions to be fulfilled in order to maximise the yield of the NA only with qualitative information. The water content should be minimised as this hydrolyses the acids and reduces the  $\text{NO}_2^+$  produced. N has to be completely dissociated to produce the maximum concentration of  $\text{NO}_2^+$  and eliminate the production of nitrophenols. A high concentration of S is required to guarantee total dissociation of N into  $\text{NO}_2^+$ . However an increase in S also increases the amount of di and trinitro aromatics as these are produced via the same mechanism.

Figure 2 shows a phenomena-based representation of this process. On the interest of the space, only the main phenomena have been represented. This representation follows the structure described in section 2.1 and is independent of equipment, in such a way that can be used to represent any process configuration. This provides visual insights useful to further identify conditions that may encourage or discourage the existence of certain phenomena. This representation shows material and balances that can be translated into equations. For this case we have used the models presented by Zaldivar, et. al. [13] and Quadros, et. al. [14]. These equations have been used to produce a VBCG (not

Hybrid modelling methodology to implement chemical process models as phenomena-based modules

5

depicted here) as presented in [1]. This model is used to analyse the effects of exogenous variables over those that directly affect the amount of NA produced.

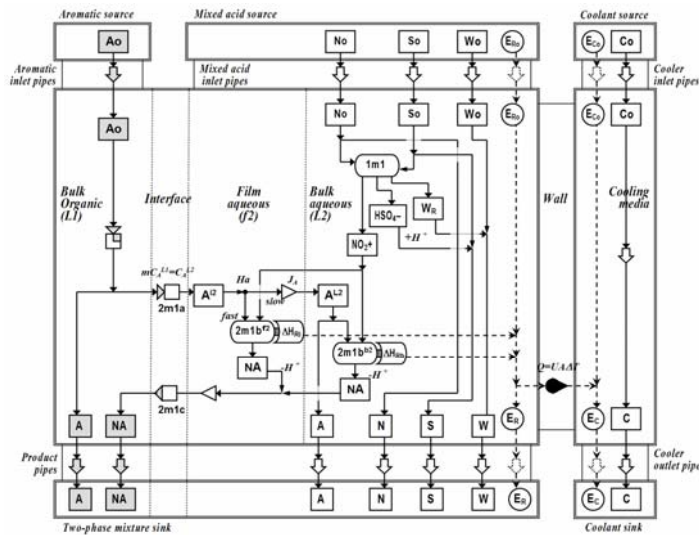


Figure 2. Phenomena-based process representation for the nitration of aromatics

### 3.2. Quantitative modelling: implementation in Aspen Custom Modeler (ACM)

The equations are grouped in modules using the hierarchy depicted in figure 3 and implemented in ACM. The primitive models are defined by the physicochemical phenomena, related to each of the symbols in figure 2. These are used to generate composite modules defining structural models. This model has been used to evaluate the effect of the S concentration and interfacial area.

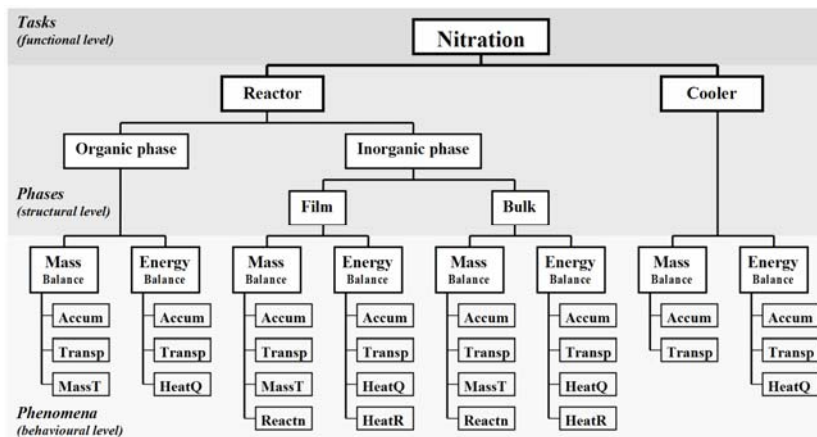


Figure 3. Model hierarchy for the implementation of phenomena-based modules in ACM

### 3.3. Results and discussions

S in a proportion higher than 80% produces considerable amounts of  $\text{NO}_2^+$  (when  $S < 80\%$ , N is dissociated into  $\text{NO}_3^-$ ). Nitrophenols are reduced; however there is a considerable increase in dinitroaromatics. Based on the Hatta number, when  $S > 80\%$  the reaction is very fast, being limited by mass transfer rates. It has been found that these are more significantly dependent on the interfacial area. The process under these conditions can be carried out in a micro reactor as studied by Burns and Ramshaw [15]. However for this case S acts only as a catalyst and occupies ~65% of the reactor volume. The size of the plant used to recover S has almost the same size than the conventional nitration equipment.

### 4. Conclusions

In this approach, the degrees of freedom are increased as the process is not constrained early to unit operations, revealing features of intensification and making explicit the associated degrees of freedom. Also, combined advantages are gained in model flexibility, customisation, reusability, complexity and cost. This approach provides increased insights and makes evident the degrees of freedom in design, expanding the heuristic rules from the early development of PI. Phenomena-based building blocks 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. 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

### References

1. Arizmendi-Sánchez, J.A., Sharratt, P.N., (PI)<sup>2</sup> conference II. 2006. Christchurch.
2. Shah, N., et al. FOCAPD 1999. Breckenbridge, USA.
3. Mangold, M., et al., Chem Eng Sci, 2002. 57: p. 4099-4116.
4. Linninger, A.A., et al., Comput Chem Eng 2000. 24(2-7): p. 591-598.
5. Gilles, E.D., Chem Eng Technol., 1998. 21(2): p. 121-132.
6. Batres, R., et al., Comput Chem Eng 2002. 26: p. 487-498.
7. Tränkle, F., et al Math Comp Modelling of Dynamical Systems, 2000. 6(3): p. 283-307.
8. Bogusch, R., et al., Comput Chem Eng, 2001. 25(7-8): p. 963-995.
9. Stephanopoulos, G., et al., Comput Chem Eng, 1990. 14(8): p. 813-846.
10. Arizmendi-Sánchez, J.A., Sharratt, P.N., Comput-Aided Chem Eng, 2005. 20A p. 901-906.
11. Abright, L.F., Hanson, C., Industrial and Laboratory Nitrations. ACS Symp. Series. 1976
12. Sharratt, P., et al., J Chem Tech and Biotech, 2003. 78: p. 156-160.
13. Zaldivar, J.M., et al., Chem Eng and Processing, 1995. 34(6): p. 543-559.
14. Quadros, P.A., et al., Chem Eng J, 2005. 108(1-2): p. 1-11.
15. Burns, J.R., Ramshaw, C., Chem Eng Res Des, 1999. 77(3): p. 206-211