A MODELING FRAMEWORK FOR CHEMICAL PROCESS DESIGN THROUGH A COMPUTER-AIDED SYSTEM

Mauricio Sales-Cruz and Rafiqul Gani *
CAPEC, Department of Chemical engineering
Technical University of Denmark, DK-2800 Lyngby, Denmark

Abstract

This paper deals with a modeling environment for systematic chemical process design through a Computer-Aided Modeling System (CAMS), whose potential is highlighted through a case study. In particular, the capability of ICAS-MoT (an integrated modeling environment) to build, analyze, manipulate, solve and visualize mathematical models is shown. Our main interest is to use models for process design and analysis by testing and implementing them as fast as possible (in a reliable and efficient manner), writing the model equations without any programming effort, generating modules that can be exported through a model transfer feature to other simulation engines and/or external software, and implementing several process/model configurations in the same environment. From the application perspective, the modeling, operational analysis and process configuration of an emulsion polymerization reactor is considered. The case study highlights the advantages of using a computer-aided modeling system in terms of time and modeling effort.

Keywords

Computer-aided modeling system, process design, polymerization reactors.

Introduction

In recent years, chemical process modeling has dominated the research and development from a process lifecycle perspective, with the need of providing a flexible set of computer-aided tools for model development and maintenance using an integrated environment. Such modeling tools should facilitate the (re)use of modeling knowledge during the process lifecycle, since the information incorporated in the models can be easily translated for different target applications such as steady-state, dynamic simulation, process optimization or experimental design.

This paper highlights the use of a generic modeling framework for CAMS called ICAS-MoT (Sales-Cruz and Gani, 2003), which is applicable to a wide range of modeling and associated problems. In particular, the capability of ICAS-MoT to assist the model developer in the steps involving model construction, model solution, model verification and model validation will be shown through a case study. The aim of ICAS-MoT is to provide an intuitive, flexible and efficient way of integrating different aspects of the modeling needs, generating modules that can be used in another external software (via COM-object), and implementing several process/model configurations in the same environment.

From the application perspective, the modeling, operational analysis and process configuration of an emulsion copolymerization reactor is considered. Emulsion polymerization process has been selected as it is currently an important industrial process from which a great variety of polymers are produced, and as its modeling is a complex issue. Different applications of these emulsions require the formation of a continuous film with specific mechanical properties, which depend on the chemical composition of the emulsion polymer phases. However, the on-line measurement or estimation of the polymer composition is still a difficult task involving high

* To whom all correspondence should be addressed

cost of measurement and experimentation. Hence, CAMS is used to evaluate the dynamic behavior of the composition in the different emulsion phases thereby saving (reducing) time, manpower and material resources.

With the purpose of showing the value of the CAMS tools, several model/process configurations for the copolymerization reactor are implemented in the same environment, for instance, type of operation (batch, semi-batch or continuous), isothermal or non-isothermal conditions, and use of different polymer thermodynamics.

Modeling Framework

The process of mathematical model building is a trial and error procedure, as shown in Figure 1. The model developer usually repeats the steps more than once. He/She gets closer to reaching the model objectives with each cycle while, at the same time, refining the definition of the modeling purpose. The modeling approach can be subdivided into the following steps (Hangos and Cameron, 2001): problem definition, system characteristics, problem data evaluation, model construction, model solution, model verification, and model validation. Usually all of these steps consume a lot of human resources and time. However, if the work is divided between human and computer, so that the computer assists to the model developer where it is efficient and leaving to the human the parts that require important decisions, then time and cost for model development can be significantly reduced.

The modeling framework used in this work is ICAS-MoT, which is an integrated modeling environment to build, analyze, manipulate, solve and visualize mathematic models. Some important features of ICAS-MoT is that in:

(a) Model Construction: The model developer does not need to write any programming codes to enter the model equations. Models are entered (imported) as text-files or XML-files, which are then internally translated.

(b) Model Analysis: ICAS-MoT orders the equations into lower triangular form (if feasible), generates the incidence matrix, verifies the degrees of freedom, and checks for singularity.

(c) Model Solution: The appropriate solver for the model equations is selected together with a solution strategy. As solver options, ICAS-MoT provides several solvers for AEs (algebraic equations), DAEs (differential algebraic equations) and numerical optimization methods.

(d) Model Validation: ICAS-MoT permits to simulate very easily and quickly different models and/or process configurations in the same environment.

(e) Model Transfer: A COM-object of the solved model can be generated to transfer it to the ICAS library (for use through the ICAS simulation engine) and to use in external software (see figure 2, where DynSim represents the dynamic simulation engine of ICAS). A model transfer is recommended for repeated model use, for example, for different sets of parameters, compound properties, reaction kinetics and equipment sizing data.

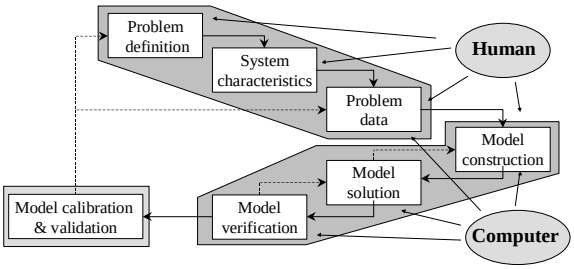

Figure 1. Modeling Framework

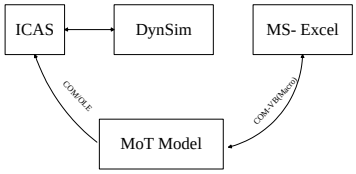

Figure 2. Model transfer through COM-Object.

Process Design: Emulsion Copolymerization Reactor

Process Description

A well-mixed tank reactor operating in batch, semi-batch, or continuous mode is considered, where an emulsion copolymerization takes place and a heating/ cooling jacket enables the heat exchange. A free-radical polymerization mechanism is considered, involving four main steps: initiation, propagation, chain transfer and termination. In the case of a copolymerization system, both monomers are activated to form free radicals, thus three initiation steps are considered with a terminal decomposing initiator. Propagation involves four distinctly different steps, neglecting penultimate effects. Termination, either by combination or disproportional reaction involves six steps, while transfer reactions can occur with a variety of chemical species including monomer, emulsifier, solvent, polymer and chain transfer agents.

Model Construction

Taking into account the preceding free-radical mechanism, the dynamic model is derived from balances of mass, volume and total energy (details of modeling and parameters can be found in Dimitratos et al. 1989):

$$\frac{d[M_1^P]}{dt} = g_1\left\{[M_1^P],[M_2^P],[I],V_R,F_1,F_2,F_{out},\alpha_1,\alpha_2\right\} \quad (1)$$

$$\frac{d[M_2^P]}{dt} = g_2\left\{[M_1^P],[M_2^P],[I],V_R,F_1,F_2,F_{out},\alpha_1,\alpha_2\right\} \quad (2)$$

$$\frac{d[I]}{dt} = g_3\left\{[M_1^P],[M_2^P],[I],V_R,F_1,F_2,F_{out},\alpha_1,\alpha_2\right\} \quad (3)$$

$$\frac{dV_R}{dt} = g_4\left\{[M_1^P],[M_2^P],[I],V_R,F_1,F_2,F_{out}\right\} \quad (4)$$

$$\frac{dT_R}{dt} = g_5\left\{[M_1^P],[M_2^P],[I],V_R,F_1,F_2,F_{out}\right\} \quad (5)$$

$$\alpha_1 = [M_1^P]/[M_1^a], \qquad \alpha_2 = [M_2^P]/[M_2^a] \quad (6)$$

Where $[M_i^p]$ and $[M_i^a]$ are the concentration of the monomer *i* in the polymeric (*p*) and aqueous (*a*) phases respectively, [*I*] is the initiator concentration, V_R is reactor volume, T_R is the reactor temperature, F_i and F_{out} are the feed and exit flow rates respectively, α_i is the partition coefficient of the monomer *i*, and g_i are nonlinear functions defined in Dimitratos et al. (1989).

In particular, the emulsion copolymerization of styrene (*S* or M_1) and methyl methacrylate (*MMA* or M_2) are considered, with ammonium and potassium persulfate as initiator. The reaction rates for initiator decomposition, for propagation, and termination are Arrhenius-type.

The model in text form is imported to ICAS-MoT, which automatically translates the model equation into a form that the computer understands.

Process/Model Configurations

With a process design perspective, three different process/model configurations are considered for the evaluation of the dynamic behavior of the monomer concentration in the emulsion:

I. Operation type: batch (i.e., $F_1 = F_2 = F_{out} = 0$), semi-batch (i.e. $F_{out} = 0$) or continuous.

II. Isothermal or non-isothermal conditions.

III. Thermodynamic model (Flory, 1953): Using constant monomer partition coefficients [Eq. (7)] or thermodynamic equilibrium for both monomers [Eq. (8)].

$$\alpha_1 = 44, \qquad \alpha_2 = 1280 \quad (7)$$

$$\Delta G_i^p\left\{[M_1^p],[M_2^p],\alpha_1,\alpha_2\right\} = \Delta G_i^a\left\{[M_1^p],[M_2^p],\alpha_1,\alpha_2\right\}, \quad i = 1,2 \quad (8)$$

Where ΔG_i^p and ΔG_i^a are the partial molar free energies of the monomer *i* in polymeric (*p*) and aqueous (*a*) phases respectively.

Model Analysis

According to ICAS-MoT, the model equations [Eqs. (1) – (6) with (7) or (8)] form a set of stiff DAEs. The classification of equations and variables is done through ICAS-MoT as follows: (a) Using constant monomer partition coefficients [Eq. (7)]: there are 89 equations (5 are ODEs and 84 are explicit AEs) with 5 dependent variables and 21 parameters, and (b) Using the thermodynamic equilibrium [Eq. (8)]: there are 91 equations (5 are ODEs, 2 are implicit AEs and 84 are explicit AEs) with 5 dependent variables, 2 unknown variables and 26 parameters.

The corresponding model parameters are given in Table 1.

Model Solution and Results

Through the solver in ICAS-MoT, dynamic simulations based on the imported model have been performed to generate an estimate of the monomer concentrations in the different phases. Note that since the imported model equations have already been translated by ICAS-MoT no further programming is necessary to use the solver. The DAE set has been solved with the BDF (Backward Difference Formula) method available in ICAS-MoT. Figures 3 - 5 show the simulated results for the dynamic behavior of the monomer concentrations in the emulsion phases for different process/model configurations.

Figure 3 shows the evolution of the monomer concentrations (in the polymeric phase) for a semi-batch reactor considering two scenarios -for isothermal conditions (showing the effect of using the thermodynamic model as well as α_i constant) and for non-isothermal case (with α_i constant). It can be seen that concentrations change throughout the polymerization process (considering monomer addition during all reaction), and a drop in the level of monomers in the polymer particles is also observed. This drop is basically due to the diffusion of

Table 1. Model Parameters for S/MMA Copolymerization

Symbol	Value	Ref
	S monomer	
MW_1	104.15	[1]
$k_{p11,o}$	$1.259\text{x}10^7$ dm^3/(mol·s)	[2]
E_{p11}	-29 kJ/mol	[2]
$k_{t11,o}$	$1.7\text{x}10^9$ dm^3/(mol·s)	[2]
$E_{t11,o}$	-9 kJ/mol	[2]
d_1	903 g/dm^3	[1]
d_{p1}	1050 g/dm^3	[1]
χ_{1p}	0.45	[3]
	MMA monomer	
MW_2	100.11	[1]
$k_{p22,o}$	$4.768\text{x}10^7$ dm^3/(mol·s)	[2]
E_{p22}/R_g	-3762 K	[2]
$k_{t22,o}$	6.581x10 dm^3/(mol·s)	[2]
E_{t22}/R_g	2536 K	[2]
d_2	930 g/dm	[1]
d_{p2}	1190 g/dm	[1]
χ_{2p}	0.30	[3]
	S/MMA copolymer	
r_1	0.501	[2]
r_2	0.472	[2]
$\chi_{12}=\chi_{21}$	0	[3]
γ	20 dyne/cm	[3]
r_p	$4.6\text{x}10^{-8}$ dm	[3]
$k_{d,o}$	$2.288\text{x}10^{16}$ s^{-1}	[2]
E_d	-137.9 kJ/mol	[2]

f	0.90	[2]

[1] Brandrup and Immergut (1989), [2] Richards and Congalidis (1989), [3] Gilbert (1995).

monomer from the aqueous phase into the polymer particles, which is modeled through the partition coefficients (Eq. 7) as well as the thermodynamic equilibrium approach (Eq. 8). Moreover this drop is more significant when the reactor is operated in non-isothermal conditions. It is worth mentioning that these simulated scenarios are also in accordance with those reported by the authors of the original model (Dimitratos et al., 1989). Figure 4 shows the isothermal monomer concentration profile (in all emulsion phases) for a batch reactor operation. As it can be seen, the concentrations decrease due to the lack of monomer addition, and the predict aqueous phase concentration does not exceed the monomer solubility (0.04 mol l^{-1}) at the reaction temperature (60 C). Finally, Figure 5 shows the isothermal monomer concentration profile (in the polymeric phase) for a continuous reactor operation, considering constant volume (0.56 l). Similar to the semi-batch operation, there is a drop in the monomer concentrations, but unlike the previous case the drop slope changes faster due to the continuous exit flowrate.

With the polymerization model verified, through ICAS-MoT, a COM-Object can be automatically generated. This COM-Object may be used in external simulation engines, it can be the basis for customized simulators, and/or used for further studies involving model identification, process optimization and experiment design.

Conclusions

The framework for a computer-aided modeling system has been presented and the modeling features related to a process design have been highlighted through a case study. An important feature of the computer-aided system is that a model representing the process/operation can be imported into ICAS-MoT system easier than most of other modeling languages, without the user having to write any programming code. This makes the usually iterative model development very efficient, fast and robust. The ICAS-MoT system also provides features for model analysis and model export in the form of COM-objects that can be used through external software, allows the creation of customized computer-aided systems. Furthermore, the results illustrate that through the use of a modeling framework with features to understand the main characteristics of chemical processes, as well as to implement different process configurations in the same simulation environment, saves time in the cycle of modeling activities. ICAS-MoT has also been tested with a collection of process models from industry and from open literature.

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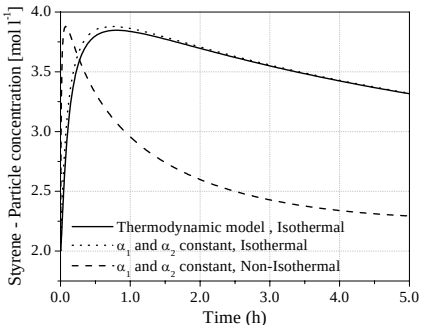

Figure 3. Styrene concentrations in semi-batch operation for: isothermal (different thermodynamics) and non-isothermal conditions (α_i constant).

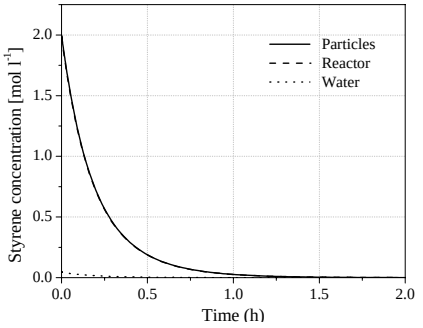

Figure 4. Styrene concentration in batch operation.

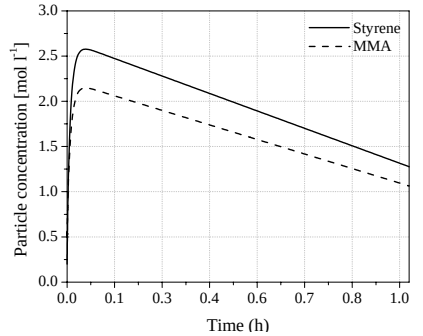

Figure 5. Particle concentrations in continuous operation.