

DYNAMIC SIMULATION OF RADICAL POLYMERISATION REACTORS IN AN OBJECT ORIENTED ENVIRONMENT

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Abstract : The aim of our ongoing study is the development of a dynamic process simulator for radical polymerisation reactors. To ensure openness, extensibility and reusability, the simulator is developed in an object-oriented environment. The modelling approach is general and applicable for widely used free radical polymerisation reactors. The range of applications of the simulator includes the prediction of the product characteristics based on molecular weight averages depending on process design, operation and additives. This paper takes a tubular polymerisation reactor for polystyrene (PS) as an example.

Keywords : polymerisation reactor, tubular reactor, dynamic simulation, Object-Oriented Analysis and Design

Introduction

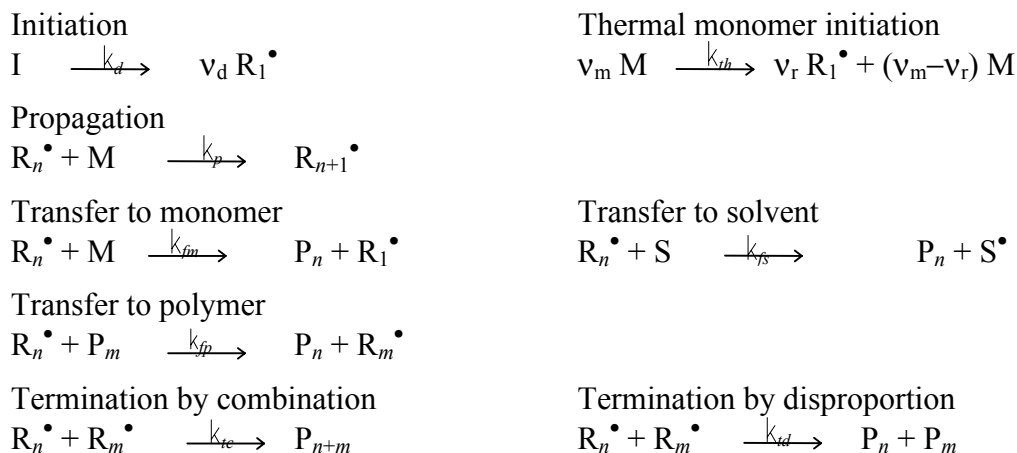
As polymers are important industrial products, there is a growing need for detailed and flexible simulation of phenomena taking place in polymerisation reactors, in particular in the so called radical polymerisation reactors.

Polymerisation raises some interesting points. In the first place, the number of chemical species participating in polymerisation reactions is potentially infinite, and the rigorous mathematical description of the dynamic behaviour of the reactor would require an extremely large set of differential equations. Then, viscosity increases dramatically with molecular weight and polymer concentration. It is typically 10^4 to 10^7 times higher than for ordinary liquids. Molecular diffusivities in polymer solutions are accordingly lowered by a factor of 10 to 10^4 . Laminar flow is the rule; pressure drops are high; agitation difficult and heat and mass transfer limitations can be severe. Thus, a specific thermodynamic property and reactor modelling tool is necessary.

The object-oriented environment offers new possibilities to reach a more general and reusable structure for process simulators. On the basis of this philosophy, a dynamic model for free radical chain growth polymerisation has been developed. The resulting simulator is able to represent the behaviour of continuous stirred-tank and tubular reactors.

Reaction Mechanism

Macromolecular architecture of a polymer depends heavily on the reaction mechanism involved. The reaction mechanism adopted in this study includes decomposition of mono and bi-functional initiators, thermal monomer initiation, propagation, chain transfer to monomer, to solvent and polymer. It accounts for side reactions involving a chain transfer agent. These reactions are relevant in industrial applications since through them the average length of the polymer product is controlled. The reaction scheme includes also termination by combination and disproportionation reactions. Such a reaction scheme will result in linear polymer chains. Branching can only occur by chain transfer to polymer reaction. This latter reaction is neglected for PS as no kinetic data is available. The polymer produced is consequently linear. The reaction scheme may be represented as follows :



where R_n^\bullet indicates a radical chain of length n, P_m relates to dead polymer of chain length m, M to monomer, I to initiator, S to solvent or to a chain transfer agent. v are reaction stoichiometric coefficients.

Reactor Modelling

The rigorous modelling based on a mass balance for every occurring specie leads to population balance equations which describe the time evolution of each individual of the population in terms of the polymer chain length. This model results in a system of ordinary differential equations whose dimension is directly related to the length of polymer chains, which can be as large as 10^4 to 10^5 . As the direct solution of this equation system is impractical, several numerical techniques have been adopted in practice, namely the widely used method of moments [1] and the discrete weighted residual methods, such as the Galerkin method presented by Canu and Ray [2] or Budde and Wulkow [3]. In this paper the method of moments is used. This approach allows a rather simple and fine discretization of the tubular reactor. The moment expressions are derived from the population balance by using the associated generating function. The number-average, weight-average and z-average molecular weights M_n , M_w and M_z are defined as the ratio of the zero to fourth order moments.

The modelling of the overall behaviour of the reactor is based on monomer conversion. This permits to uncouple the computation of monomer conversion, including the evolution of the initiator and solvent concentration, from the computation of average molecular weights carried out in a second step. The reactor model equations are written in a general form. For the tube side of a tubular reactor, the total mass, partial mass and the heat balance can be translated in the following equations :

Global mass balance

$$\frac{\partial \dot{V} C}{\partial V} + \Gamma \frac{\partial^2 (\dot{V} C)}{\partial V^2} + \sum_{i,j} v_{i,j} r_j - \frac{\partial C}{\partial t} = 0 \quad (1)$$

Partial mass balance

$$\frac{\partial (\dot{V} C x_i)}{\partial V} + \Gamma \frac{\partial^2 (\dot{V} C x_i)}{\partial V^2} + \sum_j v_{i,j} r_j - \frac{\partial (C x_i)}{\partial t} = 0 \quad (2)$$

Heat balance

$$\frac{\partial (\dot{V} C H)}{\partial V} + \Gamma \frac{\partial^2 (\dot{V} C H)}{\partial V^2} + \frac{\partial Q_{cool}}{\partial V} + \sum_j r_j \Delta H_{reac} = \frac{\partial (C H)}{\partial t} \quad (3)$$

The indices i represents the monomer, the solvent, the initiator and the pseudo components such as polymer and radical.

The dispersion coefficient Γ is a simple way to take into account the finite mass transfer arising from non plug flow in a tubular reactor. To solve the partial differential equations system, the model is discretized in space by a finite volume method. A series of perfectly stirred tank reactor models is obtained. The grid spacing can be selected from the *Péclet* number (Pe), such that the grid spacing becomes larger with increasing diffusion (decreasing Pe number).

High flexibility is guaranteed through the kit like structure of the different models. This allows the hierarchical decomposition of individual process units into physically meaningful, finer grained modelling entities on a lower level such it was described in Marquardt [4]. Here the object oriented analysis and design is based on the work of Jourda *et al.* [5] and Moyse *et al.* [6] who propose an object oriented framework for dynamic process simulation. In the first modelling step, a tubular reactor is discretized in space. It gives reactor slices of length Δz . In a second step, a reactor slice is separated into an inner fluid, an inner wall, an outer fluid and an outer wall as shown in Figure 1. A fluid is characterised by its phase system, its geometry and, if present, by its reaction system. A wall is characterised by its material and a geometry.

Every fluid element has material input and output ports as well as an energy output port. In addition the polymer fluid element has input and output information ports to transmit the first to third order moments of the molecular weight distribution (MWD) from one fluid element to the other. The inner wall has two input energy ports. The process is defined by connecting an input port to an output port, hence allowing a simple modelling of a counter- or a co-current tubular reactor. For this reason, flow direction in the outer fluid slice is not imposed in Figure 1.

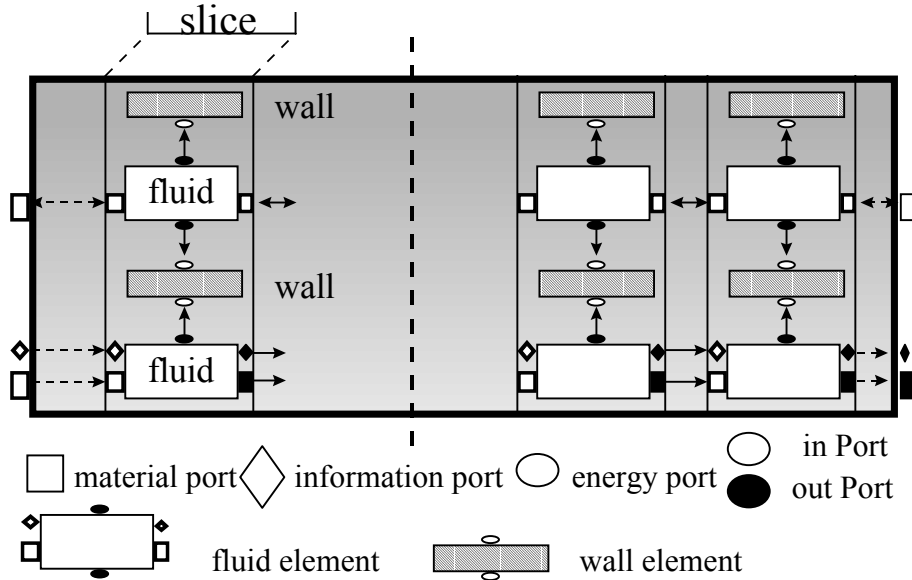


Figure 1 : *Discretisation and decomposition of a tubular polymerisation reactor*

For the inner fluid where a polymerisation reaction takes place, the discretized total mass, partial mass and the heat balance for one fluid slice are given by:

Global material balance

$$\dot{V}_f C_f + V \sum_{i,j} v_{i,j} \mathfrak{R}_j - \dot{V}_e C_e - \frac{\partial(V C_e)}{\partial t} = 0 \quad (4)$$

Partial material balance of component i

$$\dot{V}_f C_f x_{i,f} + V \sum_j v_{i,j} \mathfrak{R}_j - \dot{V}_e C_e x_{i,e} - \frac{\partial(V C_e x_{i,e})}{\partial t} = 0 \quad (5)$$

Heat balance

$$\dot{V}_f C_f H_f + V \sum_j \mathfrak{R}_j \Delta H_{\text{reac}} - \dot{V}_e C_e H_e + Q_{\text{wall}} - \frac{\partial(V C_e H_e)}{\partial t} = 0 \quad (6)$$

Reactor volume constraint

$$\dot{V}_f \rho_f(x_{i,f}, T_f, P_f) - \dot{V}_e \rho_e(x_{i,e}, T_e, P_e) - \frac{\partial(V \rho_e)}{\partial t} = 0 \quad (7)$$

Enthalpy model

$$H_e - mH(T_e, x_{i,e}, P_e) = 0 \quad (8)$$

Heat exchange model

$$Q_{\text{wall}} - mQ_{\text{wall}}(T_e, T_{\text{wall}}, \dot{V}, x_{i,e}) = 0 \quad (9)$$

Partial reaction rate model

$$\mathfrak{R}_j - m\mathfrak{R}_j(T_e, x_{i,e}) = 0 \quad (10)$$

Pressure drop model

$$(P_e - P_f) - m\Delta P(T_e, x_{i,e}, \dot{V}_e) = 0 \quad (11)$$

where mH , mr_i , $m\Delta P$ and mQ represent respectively the enthalpy, kinetic, pressure drop and heat transfer models.

The outer fluid slice contains a material system without any reaction. Therefore, the partial material balances and the partial reaction rate model are ignored to model the outer fluid slice.

Polymer Characterisation

Due to its heterogeneous composition, polymer systems cannot be defined on the basis of pseudo pure components. Further information is necessary to describe entirely the properties of a polymer. In general, the hierarchical characterisation of polymers can be described as in the lower part of Figure 2. In essence, the physical properties of polymers are defined by two fundamental characteristics: their chemical structure and their molecular weight distribution (MWD) pattern. For most thermoplastics and engineering plastics the MWD is reasonably well described when the number-average, weight-average and z-average molecular weights M_n , M_w and M_z are known. For branched polymers, a branching degree should further be computed. Polymers are characterised through polymer reaction mechanism, type of polymerisation process and reactor type as illustrated in the upper part of Figure 2.

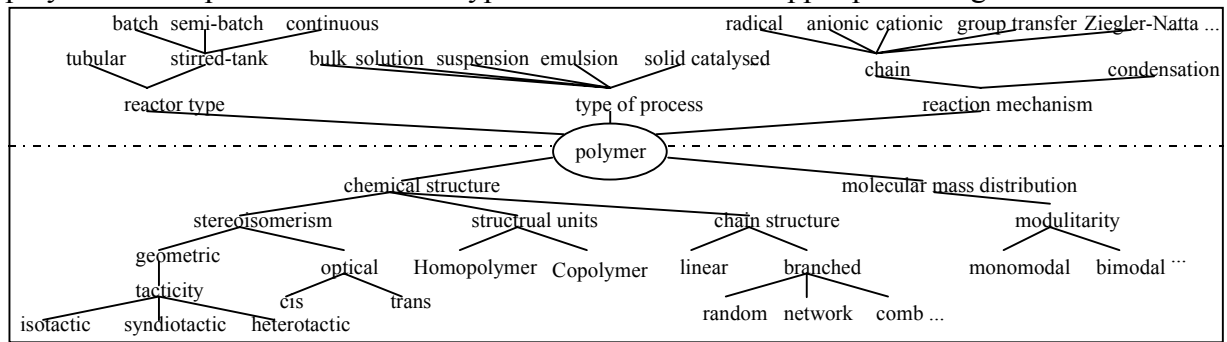


Figure 2 : Characterisation of polymers

Thus the molecular weight distribution of the produced polymer is calculated from zero to third order moments. The moment balance is formulated using the principle of conservation of moments. This principle applied on the four different moments is represented by the partial material balance equations applied on the moments.

Partial moment balance of moment i :

$$\dot{V}_f \mu_{i,f} + V \mathfrak{R}_{\mu_i} - \dot{V}_e \mu_{i,e} - \frac{\partial (V \mu_{i,e})}{\partial t} = 0 \quad i = 0, \dots, 3 \quad (12)$$

Moment reaction rate model

$$\mathfrak{R}_{\mu_i} - m\mathfrak{R}_{\mu_i}(T_e, x_{i,e}) = 0 \quad (13)$$

Various models have been developed to define the moment reaction rates \mathfrak{R}_{μ_i} . A general expression can be found in Fiorentino *et al.* [7]. In our study the moment reaction rates are based on the expressions found in Hui and Hamielec [8] developed for the polystyrene polymerisation.

The quasi-steady-state approximation (QSSA) which can be interpreted as an instantaneous and dynamically changing equilibrium between the formation and the termination of radicals is not applied.

Implementation and mathematical resolution

As it is well-known, object oriented technology offers many advantages to programmers, principally inheritance, polymorphism and dynamic linking. The principle of reusing existing structures is made possible by the concept of inheritance (is-a relationship) and aggregation (has-a relationship). Object-oriented technology allows to build a software tool with a modular structure which permits to implement the model of reactor shown above. Object technology is also applied in the ongoing CAPE-OPEN Brite-Euram project which aims to define standard interfaces for process simulation tools [9]. In our study, as well as in CAPE-OPEN, the analysis and modelling language UML (Unified Modelling Language), in combination with C++, has been chosen for implementation. The representation of a tubular reactor translated to UML is shown in Figure 3. The grey classes are the model and material classes. The polymer tubular reactor has been introduced as a specialisation of a tubular reactor. The polymer fluid element contains a polymer phase system including the different polymer reactions and the corresponding model to calculate the polymer product characteristics. In addition, the polymer fluid element has an information input and output port to transport the zero to third order moments necessary for equation 11.

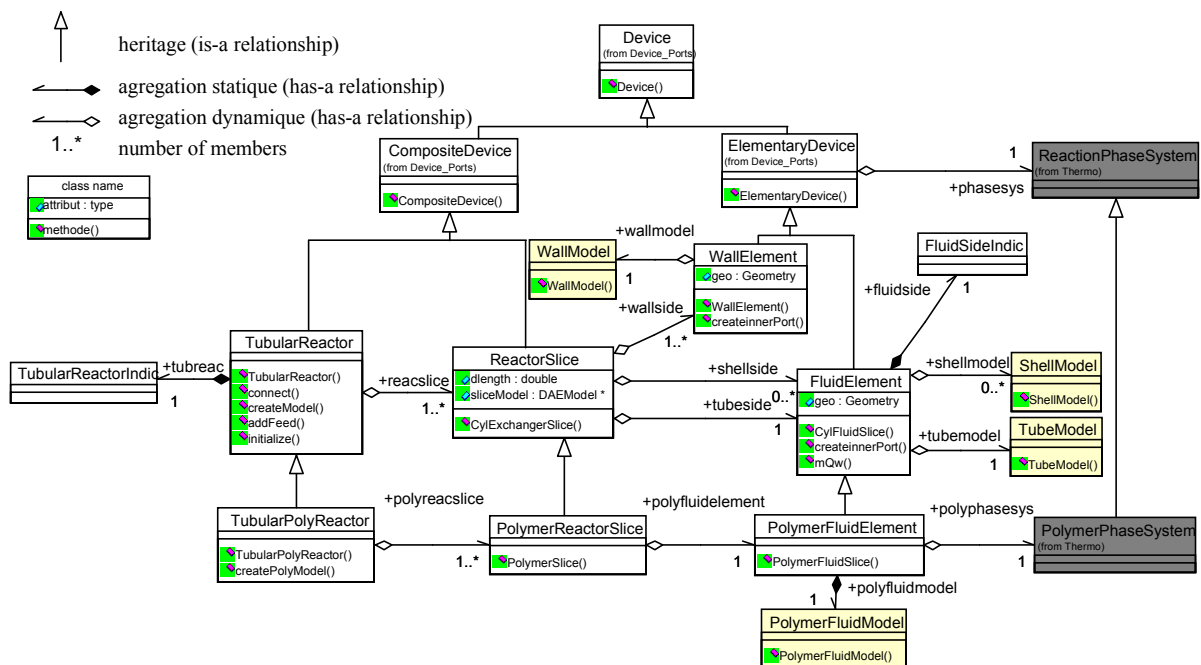


Figure 3 : Simplified UML-Diagram of the tubular polymerisation reactor

The object-oriented environment based on the thermodynamique framework ATOM [5] which is interphased to the thermodynamic library ProPhy of ProSim [10] and to the object-oriented integration software component DISCo. DISCo is described by Sargousse *et al.* [11]. It solves DAE (Differential Algebraic Equations) systems. DISCo defines variables, equations and elementary models. Each elementary model and equation is a class which inherits from an abstract class and it can be instantiated several times. The modular structure is provided by the possibility of merging elementary models to the process model, hence allowing to easily pile up the different decomposed element models. All instanciated equations and variables of each elementary model are then collected in a container class and the system is globally solved.

The simulation process can be divided into three steps. In the first step, the process has to be configured (e.g. type of process, occurring reaction etc.). Then, based on this specification, the required models including their corresponding variables are created. For a coaxial tubular

polymerisation reactor, this means that, for every discretized element, reactor, wall, cooling and moment model objects, each with their respective variables, are build and the created ports are connected. In the third and last step, process variables are initialised and the system of equations is handed to the integrator to perform simulation.

Results

As no experimental information about the dynamic behaviour of the process is available, the validation of the model is based on the process variables at steady-state. Moreover, only data on the temperature profile along the inner reactor side and the entrance temperature of the cooling fluid are available. Conversion and polymer characteristics are measured at the exit of the reactor. The validation is based on the measured global conversion X , the number average chain length M_n and the weight average chain length M_w at the reactor exit. It has been shown that, for a given temperature profile, the conversion is simulated with less than 10 % of relative error. The molecular weight average calculations are less precise. This is due to a greater sensibility to process conditions like maldistribution, as well as to local hot spots

After validation of the tubular polymerisation reactor model, the system response to a step function is investigated. In Figure 4, the evolution of conversion along the reactor at different time within the reactor is shown when the inlet polymer weight fraction is increased from 0 to 0.15. In Figure 5, the quantity of heat removed to remain at isothermal condition after decreasing the initial polymer weight fraction from 0.15 to 0, is illustrated in terms of time and location.

CONCLUSION

The structure of the process simulator allows the extensibility, reusability and openness of the simulation tool. The hierarchical decomposition of the reactor through its model allows an easy representation of the coaxial tubular reactor. High flexibility is achieved through the advantages given by object-technology and the concept of ports. The process simulator is developed in the philosophy of the ongoing CAPE-OPEN project. This will allow an easy adaptation to the defined standard interfaces.

The model equation have been presented for the inner tubular polymerisation reactor and the simulation has been validated for the process side. In the near future, heat exchange to the cooling fluid will be simulated to analyse the dynamic thermal behaviour of the reactor allowing a better understanding of the delicate control of such a reactor.

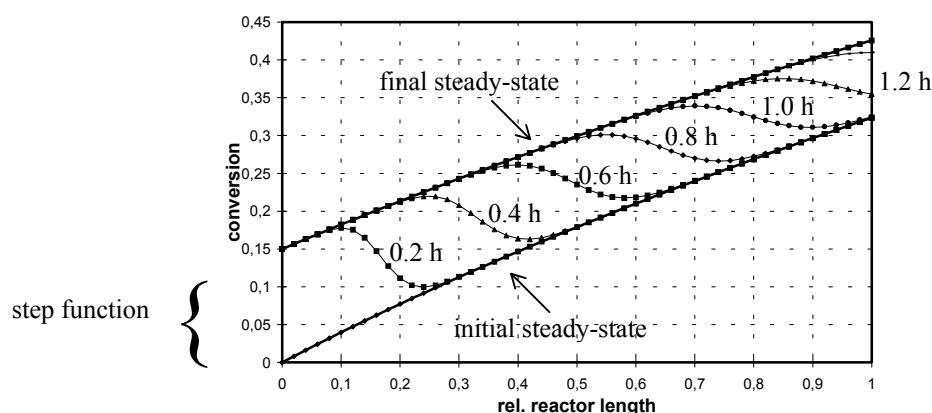


Figure 4 : Evolution of conversion after a step function on feed reactor concentration

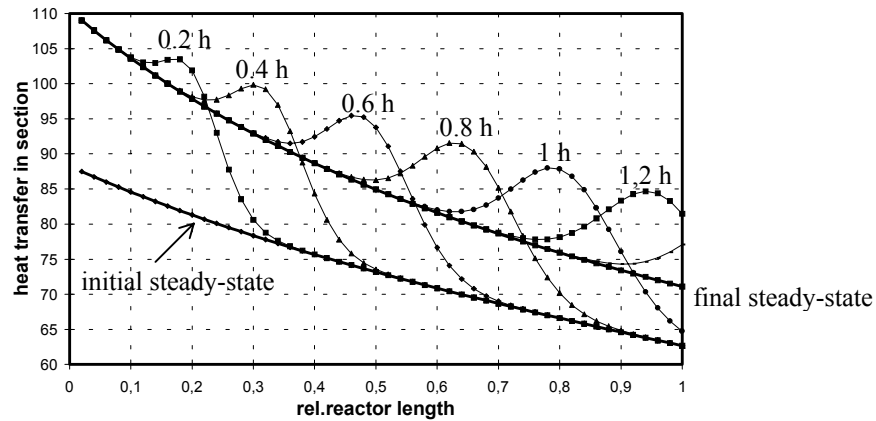


Figure 5 : Evolution of heat transfer to remain isotherm after step function on feed reactor concentration

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Nomenclature

C = total concentration [kmol/m^3]

H = enthalpy [kJ/kmol]

P = pressure

Q = heat exchange [kJ/h]

T = temperature

\dot{V} = volume flow rate [m^3/h]

V = volume [m^3]

x = molar fraction [kmol/kmol]

ΔH_{reac} = reaction heat [kJ/kmol]

ρ = density [kg/m^3]

μ_i = moment of i^{th} order

ν = stoichiometric factor

\mathfrak{R} = reaction rate [$\text{kmol}/\text{m}^3/\text{h}$]

indices

j = reaction

i = specie

f = feed

e = exit

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