Detailed Modeling of an Industrial Process: Vinyl Acetate Emulsion Homopolymerization

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Radical emulsion polymerizations are a class of fast and exothermic reactions widely diffused around the world to produce a great variety of paints and plastics. At industrial scale, repeatability of emulsion polymerization processes within narrow limits is highly desirable; this means that final solids content, particles size, emulsion viscosity and polymer average molecular weight should vary little from batch to batch. Moreover, the process should be completed in the shortest possible time and preparing a latex at the highest possible concentration to save time in production. Because of all these critical features, a reliable modeling of such processes would be very helpful at industrial scale.

In this work, a detailed model of emulsion polymerization, accounting for dosing strategies, temperature control modes, volume variations, radical diffusion (inside and outside the micelle/polymer particles) and different mechanisms of particles nucleation, is developed. A non-stationary numerical approach based onto the Smith-Ewart (SE) theory has been employed to compute the average number of radicals per particle. Finally, a series of experiments on the emulsion polymerization of vinyl acetate has been carried out in an indirectly cooled semibatch reactor (RC1, 1 L, Mettler Toledo) to validate the model.

Results have shown that, when the reactor operates under conditions (e.g., temperatures and dosing times) at which the cooling system is not able to remove all the power released by the polymerization reaction, the non-stationary approach based on the numerical solution of the Smith-Ewart equations is able to predict reactor temperature vs. time and monomer conversion vs. time profiles in a more accurate way than the stationary analytical solution of the SE equations does.

1. Introduction

Free radical emulsion polymerizations are very popular reactions used to manufacture a great variety of latexes free of flammable or toxic solvents and easy to be used because of their high fluidity (Erbil, 2000). Unfortunately, polymerizations are also known to be one of the most frequent causes of thermal runaway (that is a loss of the reactor temperature control occurring whenever the rate at which the cooling system removes heat is lower than the rate at which the heat is evolved by the exothermic reactions occurring into the reactor (Hugo and Steinbach, 1986; Alós et al., 1998; Varma et al., 1999; Zaldívar et al., 2003; Ampelli at al., 2004, 2006; Westerterp and Molga, 2006; Copelli et al., 2012, 2013a, 2013b, 2013c)) in fine chemical industries (Nolan and Barton, 1987) because of three main reasons:

1) high reaction enthalpies (up to 110 kJ/mol) and fast reaction kinetics are involved;
2) free radicals accumulation can cause sudden propagation reaction rate acceleration (Trommsdorff or gel effect);
3) boiling phenomena followed by stable foam formation can occur.

Concerning safety aspects in industrial plants, fast and strongly exothermic polymerizations are often carried out in semibatch reactors (SBRs), where the heat released is controlled by the rate at which a reactant is dosed therefore providing a low accumulation level (Copelli et al., 2011a, 2011b).

Obtaining such conditions is fundamental for the safe operation of a polymerization reactor. As a matter of fact, if a loss of temperature control would occur, dangerous boiling phenomena with consequent stable foam formation and undesired side reactions (that affect both process safety and productivity) may be triggered. Moreover, if cross-linking phenomena are induced because of the high temperature values reached during the runaway, a carbonization of the whole reacting mixture may occur. Such a phenomenon is undesired because it implies the irreparable loss of the reactor body.

On the contrary, concerning quality aspects at industrial scale, the repeatability of a polymerization process within narrow limits is always desirable; this means that final solids content should be constant within ±1%, particles size, emulsion viscosity and polymer average molecular weight should vary little from batch to batch and residual monomer should be maintained under 0.5 %. In addition, the process should be completed in the shortest possible time (8–12 h) and preparing a latex at the highest possible concentration (up to 55 % w/w) to save time in production.

Because of these critical features, a detailed modeling of such processes at industrial scale is very difficult to perform (Šoljić et al., 2009). In this work, a mathematical model able to simulate runaway operating conditions in a full-scale semibatch reactor is developed. A non-stationary numerical approach based onto the Smith and Ewart theory has been employed to compute the average number of radicals per particle. Such information is fundamental to correctly describe the system dynamics during upset operating conditions involving fast and huge thermal effects (e.g., runaway events). The corresponding population balance equations are then complemented by a suitable system of ordinary differential equations describing dosing strategies, temperature control modes, density and volume variations, material balances, jacket and reactor energy balances, radical diffusion, homogeneous and micellar nucleation phenomena. The model has been validated through experimental tests on the emulsion polymerization of vinyl acetate, carried out in an indirectly cooled semibatch reactor (RC1, 1 L, Mettler Toledo) operated in the isoperibolic temperature control mode. Obtained results have also shown that the non-stationary numerical approach adopted for the modeling is much more reliable then the corresponding stationary analytical one when it is desired to simulate the reactor thermal behavior (temperature and conversion vs. time profiles) under runaway conditions.

2. Experimental Setup

2.1 Reacting System

In order to perform a laboratory synthesis which is as close as possible to that one carried out at industrial scale, an RC1 equipment (MP06, 1 L, Mettler Toledo), indirectly cooled by means of an external jacket, has been used with the following experimental procedure (Copelli et al., 2011c): (1) distilled water (W, continuous medium), sodium lauryl sulfate (SLS, surfactant) and sodium carbonate (Na_2CO_3, buffer) are loaded into the reactor and, then, heated up to 80 °C in 40 min activating an isothermal temperature control mode; (2) the mixture is kept at 80 °C for 1 h in order to permit the formation of the SLS micelles; (3) succesively, potassium persulphate (KPS) is loaded one-shot, using an automatic syringe, into the reactor and, then, the temperature control mode is shifted to isoperibolic ($T_{cool,set}$ = 75 °C) providing a waiting time of 15 min to allow for the reactor and jacket temperatures equilibration; (4) finally, vinyl acetate (VA) is dosed by means of an automatic pump. Reaction recipe and reactor characteristics are summarized in Table 1: note that a final solid content of about 35 % w/w is considered to approach industrial conditions (that can reach up to 55 % w/w).

Table 1: Process recipe and reactor characteristics

Initial Load g		Dosed Stream g		Cooling System
279	Water	130	Vinyl Acetate	Jacket: external ($T_{cool,set}$ = 75 °C)
2.5	SLS			Coolant: silicon oil
0.5	Na_2CO_3			Nominal Volume: 1 L
1.0	KPS			UA_0 = 2.44 W/K - UA_{ext} = 0.00375 W/K

2.2 Reaction Calorimeter (RC1)

RC1 is a laboratory reactor of 1 L capacity, equipped with an external jacket to heat or cool the reacting mixture, a thermocouple and a calibration probe, which is necessary in order to determine mass specific heat capacities (c_p) and global heat transfer coefficients (UA). The calorimeter may operate in three different temperature control modes:
- Tj-mode (RC1 software controls jacket temperature);
- Tr-mode (RC1 software controls reactor temperature);
- Ta-mode (RC1 software controls the difference between jacket and reactor temperature, this mode is usually used to simulate adiabatic conditions).
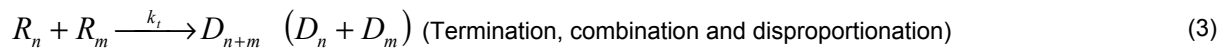
In this work, RC1 has been used in Tj-mode (in order to simulate isoperibolic operating conditions) implementing an integral-proportional action by mixing two silicon oil streams at different temperatures (low-temperature oil and high-temperature oil): this mixture is sent directly to the reactor jacket. The low-temperature oil is obtained by a cryostat circuit (T_{crio}= - 38 °C) whereas the high-temperature oil is obtained by an electrical resistance of 2 kW.

3. Theoretical Model

In this section all the equations required for the dynamic simulation of the analyzed process are reported and briefly explained.

3.1 Kinetic Scheme

The most conventional kinetic scheme for the free radical polymerization of vinyl acetate is (Erbil, 2000):
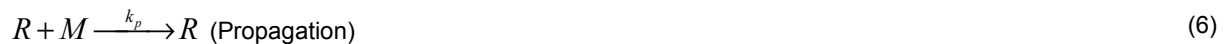
$$I_2 \xrightarrow{k_i} 2R_1 \text{ (Initiation)} \tag{1}$$

$$R_n + M \xrightarrow{k_p} R_{n+1} \text{ (Propagation)} \tag{2}$$

$$R_n + R_m \xrightarrow{k_t} D_{n+m} \ \left(D_n + D_m\right) \text{ (Termination, combination and disproportionation)} \tag{3}$$

where I is the initiator (in this case, KPS), R_n is a radical (secondary or terminal) with chain length n, M is the monomer (VA) and D_n represents a dead polymer chain with length n (chain transfer to monomer, backbiting and long-chain branching have not been considered in this work because reaction rate is the primary target of the model). Moreover, in such a simplified kinetic scheme termination by combination (tc) and by disproportionation (td) have been merged into a single contribution (t) to further decrease the number of model parameters.

Such a standard kinetic scheme has been further simplified by introducing the so-called "Terminal Kinetic Model" (TKM) approximation (Hagiopol, 1999) where a unique radical species, R:

$$R = \sum_{i=1}^{n} R_n \tag{4}$$

is considered as representative for all radicals in the reacting system independently of their chain lenght.
Using this approximation, the resulting kinetic scheme is reported in the following:

$$I_2 \xrightarrow{k_i} 2R \text{ (Initiation)} \tag{5}$$

$$R + M \xrightarrow{k_p} R \text{ (Propagation)} \tag{6}$$

$$2R \xrightarrow{k_t} D \ \left(2D\right) \text{ (Termination, combination and disproportionation)} \tag{7}$$

where D, in Eq(7), represents the generic dead polymer chain in which the effects of branching have been disregarded and no molecular weight distribution analysis has been considered according to the TKM theory.

3.2 Polymer Particle Growth and Average Number of Radicals per Particle

In an emulsion polymerization process, various chemical and physical events occur simultaneously during particle formation and growth. Particularly, particles formation takes place when (Nomura et al., 2005): (1) an active chain

in aqueous phase enters a monomer-swollen emulsifier micelle and propagation proceeds therein (micellar nucleation); (2) the length of an active chain in the aqueous phase exceeds its solubility limit (for vinyl acetate, this corresponds to about 5-7 monomer units; Erbil, 2000) and precipitates to form a new particle (homogeneous nucleation), or; (3) a free radical growing in the aqueous phase enters a monomer droplet and propagation proceeds therein (droplet nucleation, not considered in this work). If the resultant polymer particles are not stable enough, their final number, N_p, is greatly reduced by coagulation between existing particles. In this work, micellar and homogeneous nucleation have been properly taken into account whereas coagulation has been neglected because a large amount of emulsifier has been employed in order to establish full coverage of the growing polymer particles. Accordingly, the following equation can be written to compute N_p:

$$\frac{dN_p}{dt} = k_{nucl,mic} \cdot [R]_w \cdot N_{mic} + k_{nucl,omo} \cdot [R]_w \cdot N_A \cdot V_w \tag{8}$$

where t is time, s; $k_{nucl,mic}$ is the micellar nucleation rate constant, m^3/(kmol s); $[R]_w$ is the molar concentration of radicals (independently of their chain length, $[R]_w = \Sigma[R_n]_w$) in water, kmol/m^3; N_{mic} is the number of micelles, -; $k_{nucl,omo}$ is the homogeneous nucleation rate constant, 1/s; N_A is the Avogadro's number, 6.02·10^{26} kmol^{-1}; V_w is the water volume (constant during the process because only the monomer is dosed), m^3.

To simulate the process of particle growth, it is necessary to consider that polymerization takes place almost exclusively into the polymer particles phase. Smith and Ewart were the first to establish a quantitative description of particles formation and growth in an emulsion polymerization process. Particularly, they evaluate the average number of free radicals segregated into a generic polymer particle, $\tilde{n}$, through the following equation:

$$\overline{n} = \sum_{n=0}^{\infty} nN_n \bigg/ \sum_{n=0}^{\infty} N_n = \sum_{n=0}^{\infty} nN_n \bigg/ N_p \tag{9}$$

with:

$$\frac{dN_n}{dt} = c_e N_{n-1} + c_d(n+1)N_{n+1} + c_t(n+2)(n+1)N_{n+2} - c_e N_n - c_d n N_n - c_t n(n-1)N_n \tag{10}$$

where N_n is the number of polymer particles containing n radical species; $c_e = k_{diff,wp}[R]_w s_p N_A$ is the entry rate of radicals from the water to the polymer particles (entry), 1/s; s_p is the polymer particle surface, m^2; $c_d = k_{diff,pw}$ is the transfer coefficient of the radicals leaving the polymer particles (desorption), 1/s; and c_t is the inverse of the characteristic time of bimolecular termination in the polymer particles, 1/s. The mechanism through which the number of polymer particles containing n radical species, N_n, varies during time is reported in Figure 1.
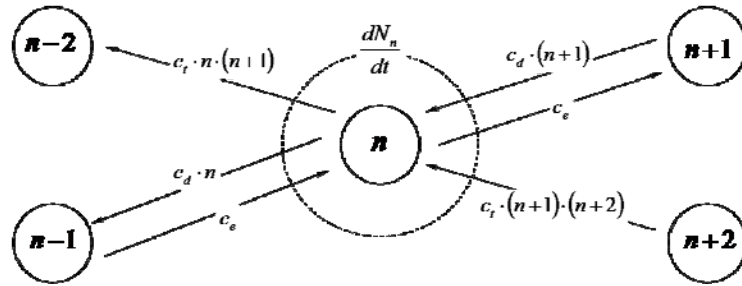

Figure 1: Mechanism of variation of the number of polymer particles containing n radical species

In order to solve Eq(10) analytically, Smith and Ewart (S-E) introduced a pseudo steady state approximation (PSSA) for N_n (that is, $dN_n/dt=0$) and neglected radical desorption obtaining the following simple expression for the total number of growing polymer particles (Nomura et al., 2005):

$$N_p = k \cdot \left(\frac{\rho_w}{\mu} \right)^{0.4} \cdot \left(a_s \cdot [E]_{w,0} \right)^{0.6} \qquad (11)$$

where k is is a constant between 0.37 and 0.53, a_s is the surface area occupied by a unit amount of emulsifier, $[E]_{w,0}$ is the initial emulsifier concentration (which is equal to the concentration of emulsifier forming micelles), μ is the volumetric growth rate per particle (see Eq(15)) and ρ_w is the rate of radical generation per unit volume of water, given by:

$$\rho_w = 2 \cdot k_i \cdot f \cdot [I]_{w,0} \qquad (12)$$

where k_i is the rate constant for initiator thermal decomposition, f is the initiator efficiency, and $[I]_{w,0}$ is the initial initiator concentration in water.

However, the complete analytical solution of Eq(9) has been found in terms of Bessel functions by Ugelstad et al. (1967) and it is given by:

$$\bar{n} = \left(\frac{a}{4} \right) \cdot \frac{I_m(a)}{I_{m-1}(a)} \qquad (13)$$

where $I_m(a)$ is the modified Bessel function of the first kind, $m = c_d v_p / c_t$, $a^2/8 = c_e v_p /(c_t N_p)$ and v_p is the actual volume of a polymer particle.

Anyway, the original equations by Smith and Ewart do not consider particle nucleations for N_n computation. In this work Eq(10) has been extended to account for nucleation phenomena (both micellar and homogeneous) and solved numerically in its non steady state version.

$$\begin{cases} n = 0 & \dfrac{dN_0}{dt} = c_d N_1 + c_t 2N_2 - c_e N_0 \\[2mm] n = 1 & \dfrac{dN_1}{dt} = c_e N_0 + c_d 2N_2 + c_t 6N_3 - c_e N_1 - c_d N_1 + k_{nucl,mic}[R]_w N_{mic} + k_{nucl,omo}[R]_w N_A V_w \\[2mm] n = 2 & \dfrac{dN_2}{dt} = c_e N_1 + c_d 3N_3 + c_t 12N_4 - c_e N_2 - c_d 2N_2 - c_t 2N_2 + c_e N_4 \\[2mm] n = 3 & \dfrac{dN_3}{dt} = c_e N_2 + c_d 4N_4 - c_e N_3 - c_d 3N_3 - c_t 6N_3 \\[2mm] n = 4 & \dfrac{dN_4}{dt} = c_e N_3 - c_e N_4 - c_d 4N_4 - c_t 12N_4 \end{cases} \qquad (14)$$

Moreover, since VA is a monomer characterized by small values of $\tilde{n}$, (Nomura et al., 2005) a finite number of such equations can be considered (in this case, the maximum number of active chains per particle has been set equal to 4).

In order to "close" the set of Eq(14), a positive term $c_e N_4$ must be inserted into the third equation; in fact, since a polymer particle with 5 radicals is unlikely to be generated, when a radical enters an N_4 particle, an instantaneous bimolecular termination takes place, thus forming an N_2 particle.

Once the average number of radicals per particle has been evaluated through Eq(14) and Eq(9), the rate of volume growth (μ) for a single polymer particle can be computed by Eq(15):

$$\mu = \frac{dv_p}{dt} = k_p \cdot MW_M \cdot \left(\frac{1}{\rho_P} - \frac{1}{\rho_M} \right) \cdot \frac{\bar{n}}{N_A} \cdot [M]_p \qquad (15)$$

where k_p is the kinetic constant for propagation reaction, (m^3 s)/kmol; ρ_M and ρ_P are the monomer and polymer density, respectively, kg/m^3; MW_M is the monomer molecular weight, kg/kmol; $[M]_p$ is the monomer molar concentration into the growing polymer particle, kmol/m^3. The last term has to be calculated accounting for the partitioning of the component among the different phases. Namely, if monomer droplets are present, $[M]_p$ is equal to its saturation value ($[M]_{p,sat}$); if there are no more monomer droplets, Eq(16) has to be used.

$$[M]_p = \frac{n_{M,dos} \cdot (v_{dos} - \zeta_M)}{v_p \cdot N_p} \tag{16}$$

where $n_{M,dos}$ is the total number of dosed monomer moles, kmol; v_{dos} is the dimensionless dosed volume; ζ_M is the monomer conversion. Note that, in the last previous equation, a negligible concentration of monomer in water is assumed, even though the water solubility of VA is actually not so small (0.24 kmol/m^3).

3.3 Material Balance Equations

The proposed model must be completed by the following material balance equations for all the species present into the reacting system, that is initiator, emulsifier, active chains in water and monomer:

$$\frac{dn_I}{dt} = -r_i \cdot V_w \tag{17}$$

$$n_E - [E]_{w,sat} \cdot V_w + \frac{s_{mic} \cdot N_{mic}}{a_s} + \frac{s_p \cdot N_p}{a_s} = 0 \tag{18}$$

$$\frac{dn_{R,w}}{dt} = 2 \cdot r_i \cdot V_w - 2 \cdot r_t \cdot V_w - c_e \cdot N_p - k_{nucl,mic} \cdot [R]_w \cdot N_{mic} - k_{nucl,omo} \cdot [R]_w \cdot N_A \cdot V_w + c_d \cdot N_p \cdot \bar{n} \tag{19}$$

$$\frac{dn_M}{dt} = F_M - r_p \cdot v_p \cdot N_p \tag{20}$$

where n_I is the initiator number of moles, kmol; r_i is the rate of initiator thermal decomposition, 1/s; n_E is the emulsifier total number of moles, kmol; $[E]_{w,sat}$ is the Critical Micellar Concentration (CMC) in water, kmol/m^3; s_{mic} is the micelle surface, m^2; $n_{R,w}$ is the number of moles of radicals in water, kmol; r_t is the rate of bimolecular termination, m^3/(kmol s); n_M is the monomer number of moles, kmol; F_M is the monomer feed molar flow rate, kmol/s; r_p is the rate of propagation reaction, kmol/(m^3 s). All reaction rates are expressed in a power law form of the type: $r= A\ exp(-E/RT) \prod []$, where A is the pre-exponential factor; E is the activation energy, J/mol; R is the ideal gas constant, = 8.314 J/(mol K); $\prod$ is the productivity of all the involved reactants concentrations [].

In Eq(17) it has been hypothesised that: 1) all the initiator is present into the continuous phase (water); 2) its decomposition kinetics is not influenced by the presence of the other reactions and 3) radicals obtained by initiator decomposition remain in water until they overcome their own solubility.

Eq(18) expresses the conservation of the total number of emulsifier in the system. In fact, the emulsifier is loaded into the reactor at the beginning of the process (in order to permit the micelles formation before the monomer dosing) and no further additions are carried out later. Particularly, it can be reasonably assumed that species E is present in the following phases: water (it is solubilized in an amount equal to its saturation value, CMC), micelles (it forms the so called "monomer swollen particles" that are constituted by emulsifier, at the surface, and monomer inside) and polymer (it is absorbed at the surface of all polymer particles that contain monomer, growing radical chains and dead polymer chains). Note that in Eq(18) the concentration of emulsifier in water has been assumed as constant (equal to its CMC) for all the process duration regardless the evidence that polymer particles are continuously growing (except during the last phases of the sysnthesis). Such an approximation can be justified considering that a huge amount of emulsifier has been loaded into the reactor, therefore providing a number of micelles sufficient to cover the overall emulsifier demand during polymer particles growth. Moreover, if such a global amount of emulsifier is not enough, it is possible to correct Eq(8) by considering a suitable coagulative contribution in between the polymer particles.

Eq(19) expresses the material balance on the radical species present into the continous phase. In this equation both radical generation (by the initiator decomposition reaction) and consumption (by termination reactions) have been properly taken into account together with the diffusive contributions due to radical entry into the polymer particles and their eventually exiting. Moreover, micellar nucleation (which have been distinguished from the radical entry) and homogeneous nucleation (that is, an overcoming of the growing radical chain solubility in water) phenomena have been considered.

Finally, Eq(20) expresses the material balance onto the monomer species which is dosed into the reactor during the semibatch period of the synthesis and, after that, simply consumed by the propagation reactions occuring inside the polymer particles. Monomer consumption in water has been disregarded, according to Eq(16), because monomer solubility in water has been considered as negligible.

3.4 Energy Balance and Control Equations

Since the model here developed is aimed to predict in detail the thermal behavior of the reactor, suitable equations of energy balance (on both the cooling/heating jacket and the reacting mixture volume) and temperature control must be written.

In order to describe the jacket thermal behavior, a continous stirred tank schematization has been adopted. Such an approximation implies that the temperature of the coolant inside the jacket is uniform all over the volume and equal to the outlet coolant temperature (a variable that can be easily measured with a thermocouple). Accordingly:

$$\left(\rho_{cool} \cdot c_{p,cool} \cdot V_{cool}\right) \cdot \frac{dT_{cool}}{dt} = \rho_{cool} \cdot c_{p,cool} \cdot Q_{cool} \cdot \left(T_{cool,in} - T_{cool}\right) + UA \cdot \left(T - T_{cool}\right) \tag{21}$$

where T is the temperature, K; c_p is the mass specific heat capacity, J/(kg K); Q is the volumetric flow rate, m^3/s; UA is the global heat transfer coefficient, W/K; subscript $cool$ refers to the coolant (or jacket), subscript in refers to an inlet stream.

Concerning, the energy balance equation for the reacting mixture volume into the reactor, it includes all thermal contributions due to dosing streams, reaction, heat transfer to both cooling/heating system and environment:

$$\rho \cdot V \cdot c_{p,mix} \cdot \frac{dT}{dt} = \frac{dV_{dos}}{dt} \cdot \rho_{dos} \cdot c_{p,dos} \cdot \left(T_{dos} - T\right) + \left(-\Delta h_{rxn}\right) \cdot \frac{dn_M}{dt} - UA \cdot \left(T - T_{cool}\right) - UA_{ext} \cdot \left(T - T_{ext}\right) \tag{22}$$

where Δh_{rxn} is the molar reaction enthalpy, J/kmol; subscript dos refers to the dosing stream; subscript ext refers to ambient.

Particularly, in this reacting system, the only exothermic reaction is the propagation; therefore, only its thermal contribution has been considered in Eq(22).

Moreover, since an industrial process involves a series of control actions onto the system temperature and the dosing policy, Eq(21) and Eq(22) must be complemented by suitable equations expressing, respectively, the reactor temperature control mode (in this case, isoperibolic, meaning that the controlled variable is the coolant temperature which is set at a desired setpoint value):

$$\frac{dT_{cool,in}}{dt} = -K_p \cdot \left[\frac{dT_{cool}}{dt} - \frac{1}{K_i} \cdot \left(T_{cool,set} - T_{cool}\right) \right] \tag{23}$$

where K_p is the temperature controller static gain, -; K_i is the reset time, s; subscript set refers to the setpoint; and the dosing policy (in this case, constant feeding rate):

$$\begin{cases} \dfrac{dV_{dos}}{dt} = \dfrac{V_{TOT,dos}}{t_{dos}} & 0 \le t < t_{dos} \\[3mm] \dfrac{dV_{dos}}{dt} = 0 & t \ge t_{dos} \end{cases} \tag{24}$$

where V_{dos} is dosed volume, m^3; $V_{TOT,dos}$ is the total volume to be dosed during the process, m^3, and t_{dos} is the dosing time, s.

As it can be noticed, Eq(23) controls the outlet coolant temperature only through the manipulation of the inlet coolant temperature (this is exactly the temperature control action performed by the RC1 controller); moreover, the derivative action has been disregarded in order to permit a simple implementation of the system of ordinary differential equations.

For what concern Eq(24), a simple control equation has been used therefore avoiding to introduce further parameters related to a dosing controller (that is, neglecting the dynamics of the dosing pump).

3.5 Overall Volume and Density

In order to estimate the overall liquid volume, the following assumptions have been considered:

1) volumes can be added one to the other in order to determine the overall liquid volume (ideal liquid solution approximation);

2) densities are constant with temperature (at least for what concern the investigated temperatures range);

3) there is a volume contraction that occurs whenever a monomer unit is added to an active growing polymer chain.

The resulting volume equation can be expressed as:

$$\frac{dV}{dt} = \frac{dV_{dos}}{dt} - \alpha \cdot \left(\zeta_M \cdot \frac{dV_{dos}}{dt} + V_{dos} \cdot \frac{d\zeta_M}{dt} \right) \tag{25}$$

where V is the liquid volume, m^3; α is the volume contraction factor, -. Through Eq(25), it is possible to express the overall liquid density writing a simple global material balance onto the reacting mass. The resulting equation is:

$$\frac{d\rho}{dt} = \frac{\rho_{dos}}{V} \cdot \frac{dV_{dos}}{dt} - \frac{\rho}{V} \cdot \frac{dV}{dt} \tag{26}$$

It should be noticed that, for the purposes of this work, it is not necessary to describe in detail all the mixing rules for the determination of the volumes of all the different phases present into the system. For this reason, a simple formula such as that of Eq(25) has been adopted.

4. Experimental Results and Model Validation

The resulting model, expressed by the system of Eqs(8) - (26), has been numerically solved using the parameters listed in Table 2 and reproducing the experimental procedure presented in section 2.1. The predicted temperature and average number of radicals per particle vs. time profiles are shown in Figures 2 and 3, respectively.

Table 2: Model parameters values (from Copelli et al., 2011c)

Kinetics – Eq(4)-(6)		Diffusion and nucleation		Thermochemical properties and control parameters	
A_i	5.33 10^{15} 1/s	$k_{nucl,omo}$	7.62 1/s at 343 K	Δh_{rxn}	8.91 10^7 J/kmol
E_i	1.23 10^5 J/mol	$k_{nucl,mic}$	7.40 10^4 m^3/kmol s at 343 K	MW_M	86.09 kg/kmol
f	0.35	$k_{diff,wp}$	1.56 10^{-1} m/s at t=0 s	α	0.2153
A_p	1.48 10^7 m^3 s/kmol	$k_{diff,pw}$	1.24 10^{-2} m/s at t=0 s	K_p	6
E_p	2.07 10^4 J/mol	r_{mic}	2.50 10^{-9} m at t=0 s	K_i	600 s
A_t	3.70 10^9 m^3 s/kmol			$T_{cool,set}$	75 °C
E_t	1.33 10^4 J/mol			$c_{p,mix}$	3489 J/kmol K

In particular, the comparison between calculated and experimental temperature vs. time curves is shown in Figure 2 for three different dosing times, respectively: 10 min (*RUN1*), 15 min (*RUN2*), 30 min (*RUN3*).

Such dosing times have been chosen because they corresponds to very different reactor thermal behaviors: *RUN1* reproduces a runaway event consisting in a fluctuation of 14 °C of the reactor temperature taking place in 10 min, *RUN2* can be classified as an intermediate situation and *RUN3* depicts a safe operating condition. As it can be verified, a good agreement between theoretical results (continuous lines) and experimental data (dotted lines) is achieved in all cases.

About the average number of radicals per particle, as shown in Figure 3, quite different trends can be observed when using the analytical steady state solution of the Smith-Ewart equations and the numerical solution of Eq(10) for describing thermal behavior of *RUN1*.

Particularly, the analytical stationary solution starts from an average number of radicals per particle equal to 0 and then, from t = 20 min (corresponding to an almost reaction completion), practically overlaps the numerical solution (that starts from $\tilde{n}$ = 0, sharply increases to $\tilde{n}$ = 1 and, then, decreases until a final value of about $\tilde{n}$ = 0.1).
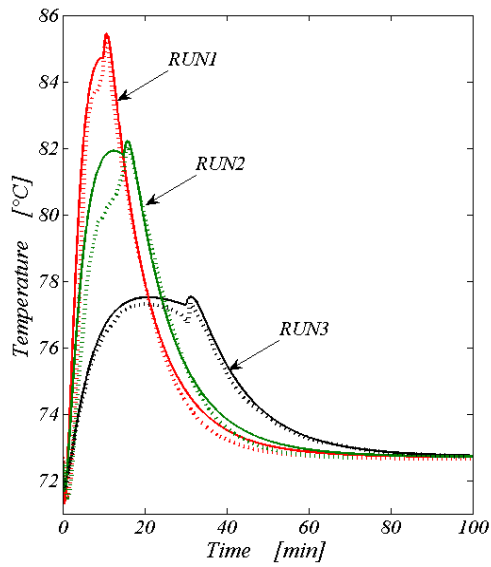
Figure 2: Comparison between experimental (dotted) and simulated (continuous) reactor temperature vs. time profiles
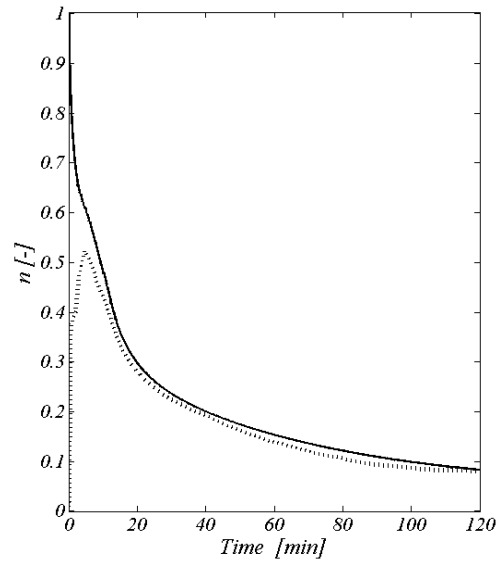
Figure 3: Comparison between analytical (dotted) and numerical (continuous) solution of S-E equation for t_{dos}=10 min (runaway conditions)

The initial disagreement between the two $\tilde{n}$ curves is responsible for the failure of the analytical stationary solution in describing the thermal behavior of the system during the runaway event (t < 20 min), as shown in Figure 4.
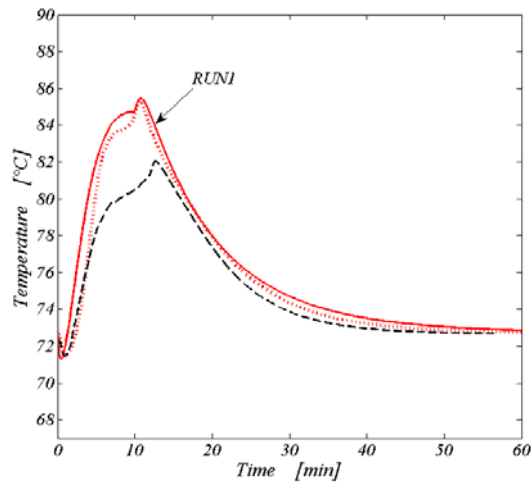

Figure 4: Comparison among experimental (red dotted), numerical simulated (red continuous) and analytical simulated (black dashed) reactor temperature vs. time profile for the RC1 test carried out using a dosing time equal to 10 min (RUN1)

In fact, during a thermal loss of control, fast variations of all state variables occur and no stationary solution should be considered to reliably describe the system thermal dynamics. In this case, the sharp temperature peak induces a strong acceleration of all kinetic and diffusion phenomena previously described leading to an instantaneous increase of the number of radicals per particle. This behavior can be correctly taken into account only using a non-stationary model. On the contrary, when the runaway event is estinguishing (t > 20 min), the stationary analytical solution can be used without loss of accuracy because it provides, substantially, the same results of the non-stationary approach.

5. Conclusions

In this work, a kinetic model of emulsion polymerization involving a non-stationary solution of the Smith-Ewart equations has been developed. The model, able to reproduce complex operational lists and control actions, such as those typical of an industrial plant, has been validated through laboratory experiments. These tests span from runaway (*RUN1*) to safe operating conditions (*RUN3*) and in all cases a good agreement between simulations and experimental data has been achieved.

Particularly, it has been demonstrated that stationary solutions should be avoided for a correct description of the real system thermal behavior whenever the system is operated under runaway conditions. This evidence has been confirmed by direct comparison of theoretical results (both from the analytical stationary and numerical unsteady state model) and experimental data.

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