

## Detailed Modelling 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 modelling 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 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.

### 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 cooling system exhibits a poor heat removal efficiency) in fine chemical industries 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.

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  $\pm 1\%$ , 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 (until 55 % w/w) to save time in production. Because of these critical features, a detailed modelling of such processes at industrial scale is very difficult to perform (Šoljić et al., 2009).

In this work, a mathematical model capable of simulating runaway operating conditions in a full plant 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.

## 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 operational procedure (Copelli et al., 2011): (1) distilled water (W, continuous medium), sodium lauryl sulfate (SLS, surfactant) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 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; (3) 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) vinyl acetate (VA) is dosed through a 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.

Table 1: Process recipe and reactor characteristics (the meaning of  $UA_0$  and  $UA_{ext}$  will be reported in section 3.4)

Initial Load		Dosed Stream		Cooling System
279 g	Water	130 g	Vinyl Acetate	Jacket: external ( $T_{cool,set} = 75$ °C)
2.5 g	SLS			Coolant: silicon oil
0.5 g	$\text{Na}_2\text{CO}_3$			Nominal Volume: 1 L
1.0 g	KPS			$UA_0 = 2.44$ W/K - $UA_{ext} = 0.00375$ W/K

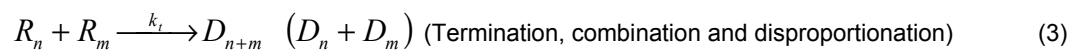
### 2.2 Reaction Calorimeter (RC1)

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 controls jacket temperature), Tr-mode (RC1 controls reactor temperature) and Ta-mode (RC1 controls the difference between jacket and reactor temperature). 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

### 3.1 Kinetic Scheme

The most conventional kinetic scheme for the free radical polymerization of vinyl acetate is (Erbil, 2000):



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 since reaction rate – and no molecular weight – 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.

### 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  $N_p$ :

$$\frac{dN_p}{dt} = k_{nucl,mic} [R]_w N_{mic} + k_{nucl,omo} [R]_w N_A V_w \quad (4)$$

where  $t$  is time, s;  $k_{nucl,mic}$  is the micellar nucleation rate constant,  $m^3/(kmol \cdot s)$ ;  $[R]_w$  is the molar concentration of radicals (of every chain length,  $[R]_w = \sum [R_n]_w$ ) 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,  $6.02 \cdot 10^{26} \text{ kmol}^{-1}$ ;  $V_w$  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,  $\bar{n}$ , through the following equation:

$$\bar{n} = \frac{\sum_{n=0}^{\infty} n N_n}{\sum_{n=0}^{\infty} N_n} = \frac{\sum_{n=0}^{\infty} n N_n}{N_p} \quad (5)$$

with:

$$\frac{dN_n}{dt} = c_e N_{n-1} + c_d (n+1) N_{n+1} + c_t (n+2)(n+1) N_{n+2} - c_e N_n - c_d n N_n - c_t n(n-1) N_n \quad (6)$$

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,  $1/s$ .

In order to solve Eq (6) 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. However, the complete analytical solution at steady state was found in terms of Bessel functions. Moreover, the original equations by Smith and Ewart do not consider particle nucleations for  $N_n$  computation. In this work Eq (6) have been extended to account for nucleation phenomena and solved numerically in their non steady state version.

$$\left\{ \begin{array}{l} n=0 \\ n=1 \\ n=2 \\ n=3 \\ n=4 \end{array} \right. \begin{array}{l} \frac{dN_0}{dt} = c_d N_1 + c_t 2N_2 - c_e N_0 \\ \frac{dN_1}{dt} = c_e N_0 + c_d 2N_2 + c_t 6N_3 - c_e N_1 - c_d N_1 + k_{nucl,mic} [R]_w N_{mic} + k_{nucl,omo} [R]_w N_A V_w \\ \frac{dN_2}{dt} = c_e N_1 + c_d 3N_3 + c_t 12N_4 - c_e N_2 - c_d 2N_2 - c_t 2N_2 + c_e N_4 \\ \frac{dN_3}{dt} = c_e N_2 + c_d 4N_4 - c_e N_3 - c_d 3N_3 - c_t 6N_3 \\ \frac{dN_4}{dt} = c_e N_3 - c_e N_4 - c_d 4N_4 - c_t 12N_4 \end{array} \quad (7)$$

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 (7), a positive term  $c_e N_4$  must be inserted into the third equation; in fact, since a polymer particle with 5 radicals is extremely 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 (7) and Eq (5), the rate of volume growth for a single polymer particle can be computed by Eq (8):

$$\frac{dv_p}{dt} = k_p MW_M \left( \frac{1}{\rho_P} - \frac{1}{\rho_M} \right) \frac{\bar{n}}{N_A} [M]_p \quad (8)$$

where  $k_p$  is the kinetic constant for propagation reaction, (m<sup>3</sup> s)/kmol;  $\rho_M$  and  $\rho_P$  are the monomer and polymer density, respectively, kg/m<sup>3</sup>;  $MW_M$  is the monomer molecular weight, kg/kmol;  $[M]_p$  is the monomer molar concentration into the growing polymer particle, kmol/m<sup>3</sup>. 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 (9) has to be used.

$$[M]_p = n_{M,dos} (v_{dos} - \zeta_M) / v_p N_p \quad (9)$$

where  $n_{M,dos}$  is the total number of dosed monomer moles, kmol;  $v_{dos}$  is the dimensionless dosed volume;  $\zeta_M$  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<sup>3</sup>).

### 3.3 Material Balance Equations

The proposed model is completed by the following material balance equations for initiator, emulsifier, active chains in water and monomer:

$$dn_i/dt = -r_i V_w \quad (10)$$

$$n_E - [E]_{w,sat} V_w + s_{mic} N_{mic} / a_s + s_p N_p / a_s = 0 \quad (11)$$

$$\frac{dn_{R,w}}{dt} = 2r_i V_w - 2r_t V_w - c_e N_p - k_{nucl,mic} [R]_w N_{mic} - k_{nucl,omo} [R]_w N_A V_w + c_d N_p \bar{n} \quad (12)$$

$$dn_M/dt = F_M - r_p v_p N_p \quad (13)$$

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<sup>3</sup>;  $s_{mic}$  is the micelle surface, m<sup>2</sup>;  $a_s$  is the total area covered by 1 kmol of emulsifier, m<sup>2</sup>/kmol;  $n_{R,w}$  is the number of moles of radicals in water, kmol;  $r_t$  is the rate of bimolecular termination, m<sup>3</sup>/(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<sup>3</sup> 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  $[ ]$ .

### 3.4 Energy Balance and Control Equations

In order to describe the jacket thermal behavior, a continuous 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. Accordingly:

$$(\rho_{cool} c_{p,cool} V_{cool}) dT_{cool}/dt = \rho_{cool} c_{p,cool} Q_{cool} (T_{cool,in} - T_{cool}) + UA(T - T_{cool}) \quad (14)$$

where  $T$  is the temperature, K;  $c_p$  is the mass specific heat capacity, J/(kg K);  $Q$  is the volumetric flow rate, m<sup>3</sup>/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.

The energy balance equation for the reactor includes all thermal contributions due to dosing streams, reaction, heat transfer to both cooling system and environment:

$$\rho V c_{p,mix} \frac{dT}{dt} = \frac{dV_{dos}}{dt} \rho_{dos} c_{p,dos} (T_{dos} - T) + (-\Delta h_{rxn}) \frac{dn_M}{dt} - UA(T - T_{cool}) - UA_{ext}(T - T_{ext}) \quad (15)$$

where  $\Delta h_{rxn}$  is the molar reaction enthalpy, J/kmol; subscript *dos* refers to the dosing stream; subscript *ext* refers to ambient.

Eq(14) and Eq(15) must be complemented by control equations expressing reactor temperature control mode (in this case, isoperibolic = constant coolant temperature):

$$dT_{cool,in}/dt = -K_p \cdot [dT_{cool}/dt - K_i^{-1} \cdot (T_{cool,set} - T_{cool})] \quad (16)$$

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) is:

$$\begin{cases} dV_{dos}/dt = V_{TOT,dos}/t_{dos} & 0 \leq t < t_{dos} \\ dV_{dos}/dt = 0 & t \geq t_{dos} \end{cases} \quad (17)$$

where  $V_{dos}$  is dosed volume, m<sup>3</sup>;  $V_{TOT,dos}$  is the total dosed volume, m<sup>3</sup>, and  $t_{dos}$  is the dosing time, s.

### 3.5 Overall Volume and Density

In order to estimate the overall liquid volume, the following assumptions are considered: 1) volume additivity law (ideal liquid solution approximation); 2) densities constant with temperature; 3) volume contraction occurring whenever a monomer unit is added to an active growing polymer chain. The resulting volume equation can be expressed as:

$$dV/dt = dV_{dos}/dt - \alpha(\zeta_M dV_{dos}/dt + V_{dos} d\zeta_M/dt) \quad (18)$$

where  $V$  is the liquid volume, m<sup>3</sup>;  $\alpha$  is the volume contraction factor, -. Through Eq (18), the overall liquid density is expressed as:

$$d\rho/dt = (\rho_{dos}/V) \cdot dV_{dos}/dt - (\rho/V) \cdot dV/dt \quad (19)$$

## 4. Results

The resulting model Eq (4)-Eq (19) have been numerically solved using the parameters listed in Table 2 and reproducing the operational procedure presented in section 2.1. The predicted temperature and average number of radicals per particle vs. time profiles are shown in Figures 1 and 2, respectively.

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

$A_i$	$5.33 \cdot 10^{19}$ (1/s)	$A_t$	$3.70 \cdot 10^9$ (m <sup>3</sup> s/kmol)	$k_{diff,svp}$	$1.56 \cdot 10^{-1}$ (m/s) at t=0 s
$E_i$	$1.23 \cdot 10^5$ (J/mol)	$E_t$	$1.33 \cdot 10^4$ (J/mol)	$k_{diff,pw}$	$1.24 \cdot 10^{-2}$ (m/s) at t=0 s
$A_p$	$1.48 \cdot 10^7$ (m <sup>3</sup> s/kmol)	$k_{nucl,omo}$	7.62 (1/s) at 343 K	$r_{mic}$	$2.50 \cdot 10^{-9}$ (m) at t=0 s
$E_p$	$2.07 \cdot 10^4$ (J/mol)	$k_{nucl,mic}$	$7.40 \cdot 10^4$ (m <sup>3</sup> /kmol s) at 343 K	$\Delta h_{rxn}$	$8.91 \cdot 10^7$ (J/kmol)

In particular, the comparison between calculated and experimental temperature vs. time curves is shown in Figure 1 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 14 °C of reactor temperature fluctuation 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 and experimental data is achieved in all cases.

About the average number of radicals per particle, quite different trends are shown in Figure 2 when using the analytical steady state solution of the Smith-Ewart equations and the numerical solution of equations (4) for describing *RUN1* thermal behavior.

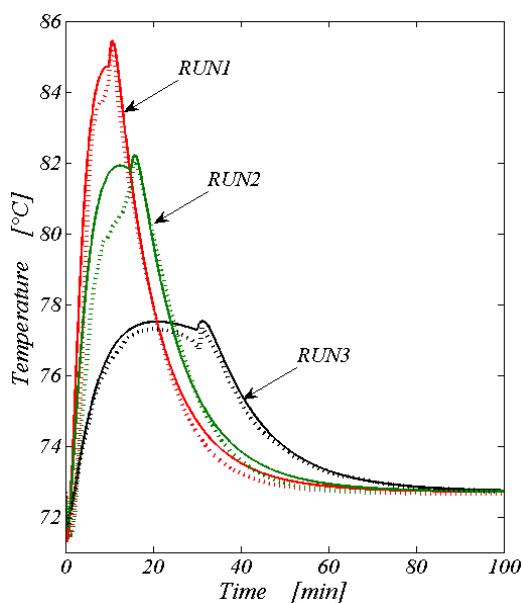


Figure 1: Comparison between experimental (dotted) and simulated (continuous) reactor temperature vs. time profiles

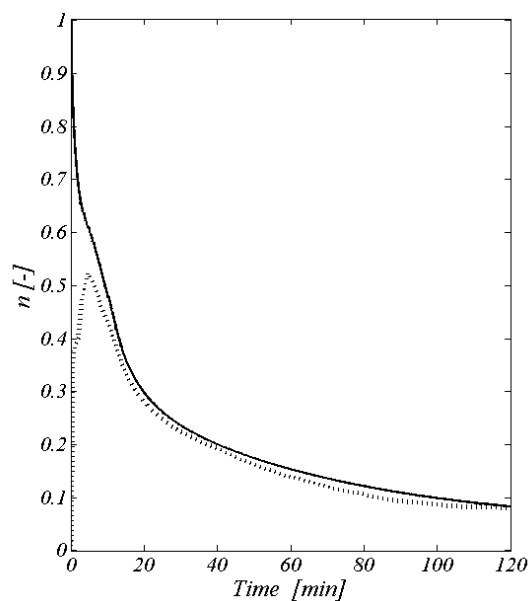


Figure 2: Comparison between analytical (dotted) and numerical (continuous) solution of S-E equation for  $t_{dos}=10$  min (runaway conditions)

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  $\bar{n} = 0$ , sharply increases to  $\bar{n} = 1$  and, then, decreases until a final value of about  $\bar{n} = 0.1$ ). The initial disagreement between the two  $\bar{n}$  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). 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 extinguishing ( $t > 20$  min), the stationary analytical solution can be used without loss of accuracy.

## 5. Conclusion

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.

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