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DYNAMIC SIMULATION OF A PVC SUSPENSION REACTOR

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ABSTRACT

The scope of this contribution is to present a comprehensive methodology for the dynamic modelling of an industrial PVC suspension reactor. The paper analyses the main features, but brings also some new insights on the polymerisation kinetics, the dynamic heat balance and the action of the control system. The model is implemented in SPEEDUPTM and can be used for the optimisation of process operation and recipe development, as well as a core component of a training simulator.

KEYWORDS

Dynamic simulation; Polymerisation, PVC, Batch Reactor

INTRODUCTION

Very large scale tank reactors, more than 100 m³, are currently used to produce PVC by suspension polymerisation. An accurate knowledge of the dynamic behaviour of the reaction system provides the means to optimise the productivity, while keeping flexibility in obtaining different polymer grades. A dynamic model of an industrial PVC reactor has been published several years ago by Dimian et al [1]. It considered a two-phase polymerisation model, time dependent heat transfer, as well as a loop cooling system driven by a PID controller. Important progress has been registered recently in modelling the polymerisation kinetics [2,3], but the scale-up from laboratory to reactor operation is still an open research problem. Recently Bretelle and Machietto [4] presented the dynamic simulation of PVC-S focused on operator training. Summing up, we may say that there is no publication devoted to a comprehensive simulation in industrial conditions. We present in this paper a complete methodological approach of this problem, bringing also some new insights on operation and scale-up.

The dynamic simulation may be applied at three levels:

- *operation*: global kinetics and thermal regime;
- *polymer quality description*: molecular weight distribution and particle morphology;
- *optimisation and improvement*: multi-initiation, non-isothermal and semi-batch operation.

Here we consider in detail the level I and briefly the level II. The model has been implemented in SPEEDUPTM [5].

REACTOR DYNAMICS

The figure 1 depicts the reactor set-up. Water and Vinyl Chloride Monomer (VCM) are loaded together with the initiator and other recipe 'ingredients'. The reaction mass is heated up to temperature T_R , that is kept constant by balancing the generated and the evacuated heat. The heating-cooling

jacket works as an overflow loop, the flowrate of the external thermal agent F_s being controlled to fulfil the reaction heat balance. An external condenser can remove the heat of polymerisation by monomer condensation. The reactor pressure is constant during the polymerisation, but shows a sharp decline after a 'critical conversion' X_c . At this point the polymerisation rate reaches its maximum and here the heat removal may be critical. The final conversion is slightly above 90%. The times to reach critical conversion τ_c and final polymerisation τ_f , respectively, are characteristic for operation. A good operation should maximise the reaction rate while respecting product specifications and a stable thermal regime.

During the polymerisation the particle morphology changes a lot, that has as consequence a complex behaviour of the suspension. A 'two phase' model has been generally accepted at the particle level. Each drop consists of a monomer-rich phase and a polymer-rich phase, swollen with monomer. A 'gel effect' will accelerate the reaction rate from the beginning up to a 'critical conversion' X_c . This complex phenomenon is essential for productivity, reactor operation and product quality. Before to start the simulation we evaluated the existing models [2,3]. The link between kinetics and particle morphology is not yet satisfactorily modelled.

Fig. 1 - Reaction system

Fig. 2 - Global kinetics

The overall heat balance of the reactor is:

$$\left(\sum M_i C_i\right) \frac{dT_R}{dt} = Q_R + Q_M - Q_t - Q_c - Q_l \quad (1)$$

where Q_R is the heat generated by reaction, Q_M is the heat generated by mixing, Q_t is the heat transmitted to the cooling system, Q_c is the heat removed by monomer condensation, Q_l is the heat loss in surroundings. Intensive heat transfer may be obtained with a channel-like jacket, where the cooling water circulates at high constant flowrate. For a long channel L of cross section ' $b \cdot h$ ' the differential heat balance gives:

$$\frac{\partial T_w}{\partial t} + w \frac{\partial T_w}{\partial z} - \frac{K}{b \rho_w C_w} (T_R - T_w) + \frac{K_l}{b \rho_w C_w} (T_w - T_m) = 0 \quad (2)$$

Neglecting the first term and integrating with the condition $z=0, T=T_{w1}$ gives the heat transferred to the cooling jacket only as function of inlet jacket temperature and the heat transfer coefficients suspension/jacket and jacket/environment.

$$Q_t = KhL \frac{K_l}{K + K_l} (T_R - T_m) - \left(T_{w1} - \frac{KT_R + K_l T_m}{K + K_l} \right) \times \frac{wb \rho_w C_w}{K + K_l} \left[1 - \exp \left(- \frac{K + K_l}{wb \rho_w C_w} L \right) \right] \quad (3)$$

The inlet jacket temperature T_{w1} is adapted continuously to heat balance requirements by injecting a thermal agent (steam for heating period, chilled water for cooling period). The controller action has to be introduced explicitly in the model. In this case a cascade configuration is appropriate because it gives a faster reaction compared with a single controller (figure 1). The PID master that controls the reactor temperature supplies the setpoint of a slave PI, which controls the inlet jacket temperature by manipulating the flowrate F_s of the external heat source.

SIMULATION RESULTS

Global kinetics

The figure 2 describes a typical simulation run, in terms of pressure, temperature, conversion and reaction rate, for Perkadox 16/40W 700 ppm at 57 °C. The shapes of these curves depend on initiator concentration and on temperature policy. A constant maximum reaction rate during the whole batch would be desirable. This might be realised by multi-initiation and programmed temperature. The kinetics modelling in this work has been done by using the general frame proposed by Xie [3] with some modifications which will be discussed below.

The computation of polymerisation rate is based on the relation:

$$N_{M_0} \frac{dX_m}{dt} = K_{p1}[R\cdot]_1[M]_1 + K_{p2}[R\cdot]_2[M]_2 \quad (4)$$

The two terms represent the rate of polymerisation in the monomer phase (1) and in the polymer phase (2), respectively. The radical concentrations $[R\cdot]_1$ and $[R\cdot]_2$ are complex functions of operating conditions, the distribution of monomer between phases and the diffusion limitations on elementary reaction steps. The fidelity of the simulation depends heavily on how the gel effect is modelled. According to the free volume theory, the rate constant of either elementary step in the polymer phase may be expressed by the equation:

$$k_2 = k_{20} \exp[-A^* (1/V_p - 1/V_{p,cr})] \quad (5)$$

where A^* is a fitting parameter, V_p is the polymer phase volume and $V_{p,cr}$ its critical value. A parametric study shows that the free volume correction accounting for diffusion effects in the polymer phase gives the highest sensitivity. The most significant conclusions are:

- The termination constant K_{t2} has a strong influence on auto acceleration effect and on polymerisation time. A variation of 10% in the critical factor gives ~20% variation in τ_c and τ_f .
- The propagation constant K_{p2} and the initiator decomposition constant K_{d2} are significant for τ_f , but without effect on auto acceleration.
- The initiator partitioning between the two phases has little influence on global kinetics.
- Critical chain length r_c of polymer radicals that precipitate is an important model parameter. A value of about 20-30 is appropriate for simulation.

The original model contains a large number of fitting parameters. However, the extrapolation in temperature and the physical meaning of some parameters are not obvious. In particular the parameter for precipitation seems to be out of bounds, requiring a critical chain length of about 3800 units. The following modifications of the Xie model have been made:

- Simplification of the free volume theory for the termination and the propagation rate constant
- Precipitation and desorption according Kuchanov [6]
- Explicit initiator balances in both phases incorporating a finite mass transfer rate
- Balance on primary polymer radicals incorporating the initiation step
- A detailed reaction network and differential balance for polymer radicals

This approach enables to examine directly the contribution of each elementary step and to modify it if necessary. The integration of approximately 250 differential equations plus the corresponding algebraic equations can be done with reasonable time in SPEEDUPTM.

The evolution of the gel effect is depicted in the figure 3 by curves displaying the number of polymer radicals in the monomer and in the polymer phase, as well as their precipitation rate. The number of macro radicals in the monomer phase reaches a maximum at a mid conversion level, falling then to zero at X_c . The number of macro radicals in the polymer phase increases continuously from zero to maximum at X_c , then drops dramatically. The precipitation rate of the macro radicals has a sharp first peak at low conversion, when the polymer aggregates are still in formation. This is followed by a significant fall, when the particle size increases. Then the precipitation rate passes through a second peak and afterwards the curve follows the decline of radicals in the monomer phase.

Another important feature in operation is the monomer balance, depicted in the figure 4. Among others, this shows that a significant amount of monomer in water exists from the beginning and up to what is considered the 'critical conversion' region. This may have two consequences in operation. Firstly, an important contribution of condensation at the critical conversion takes place, when the monomer apparently disappears as a distinct phase. Secondly, the 'critical' conversion in the industrial conditions may be higher than measured in laboratory.

Heat transfer

The basic characteristics are presented in figure 5. Early attempts have been focused on the heat transfer coefficient suspension/reactor wall. This is time variable because of the increase in suspension viscosity during polymerisation. Its computation is not accurate because of the unpredictable suspension viscosity. The figure 5 displays a realistic trend, obtained by combining the effect of increasing polymer phase with the volume shrinkage by polymerisation. Following this method the viscosity increases roughly by an order of magnitude, which can give an important reduction in the heat transfer coefficient (~30 %). The minimum value corresponds to the critical conversion where the maximum heat generation takes place. Fortunately, at this point there is monomer available to remove heat by condensation, as the monomer balance indicated. In the same time the gas cap area available for removing heat by condensation increases due to the shrinkage of the reaction volume.

The reactor wall has also an important heat resistance. When all these are added, then the overall heat transfer coefficient of the whole reactor becomes practically constant during polymerisation. Consequently, the accuracy in predicting the heat transfer coefficient of the suspension is not critical for design and operation. Both these aspects should better consider the dynamic heat balance rather than the static heat transfer contributions.

Heat balance and Temperature control

The figure 6 presents typical dynamic reactor heat balance. The reaction heat development follows the polymerisation rate. The reactor curve lumps all the contributions. The control system can keep the heat balance within an accumulation term less than 1%. The graph displays a situation where some unbalance exists: at the beginning of the batch, when the temperature exhibits an overshoot, and at the critical conversion, when the control cannot follow the auto acceleration effect. In the last case there is a 'hot spot' with a runaway tendency, that drops out by the depletion of the monomer phase.

The figure 7 illustrates the behaviour of the cooling loop by the inlet jacket temperature and the flowrate of the thermal agent. In a normal run the temperature may be kept constant within ± 0.5 C. The jacket temperature and the flow rate of the thermal agent show a mirror-like trend. When the cooling capacity is below the generated heat, for example as a consequence of polymer deposit on wall, the hot spot occurs and F_c goes through violent variations. This event may affect the reactor operation, but can be even more harmful for the product quality, by its influence on the instantaneous MWD, by more low molecular chains or by chain degradation reactions.

Molecular weight distribution

The development of the molecular weight distribution (MWD) takes place both in monomer as in polymer phase. Number-averaged, weight-averaged MWD, instantaneous and cumulative, as well as the polydispersity index can be calculated from the kinetic model, using the moment methods or by direct integration of differential equations for polymer species. This is possible with reasonable time in SPEEDUP™. In this case chain transfer, branching and any other type of reactions affecting the polymer weight distribution may be easier introduced in the kinetic scheme. Some of these steps, not essential for polymerisation rate, may become important for predicting end-product quality, especially at high conversions.

The development of instantaneous Molecular Weight Distribution (MWD) is presented in a 3D plot in the figure 8. Initially shorter length chains are formed in the monomer phase than in the polymer phase, where the termination rate is affected by the gel effect. The initial polydispersity index is slightly greater than 1.5. Then the mean molecular weight will increase, because of the greater contribution of the polymer phase. However, up to the critical conversion the polydispersity will be practically constant and close to 2, being controlled by the chain transfer to monomer. After the critical conversion the situation changes significantly. The instantaneous MWD shifts sharply again to lower values, this time because of the diffusion controlled chain transfer, not only with the monomer, but also with the polymer. The M_w will decrease slower than M_n , producing an increase in the polydispersity index. However, these important changes affect only slightly the cumulative MWD.

CONCLUSIONS

The paper presents a comprehensive dynamic modelling of a large scale suspension PVC reactor, by combining reaction kinetics, heat transfer dynamics and control system action. Typical results illustrate the approach. The kinetics remains the key factor. The recent model of Xie offers a good frame to describe both the global rate and the molecular weight distribution. However, the model is complex and very sensitive regarding some parameters. Simpler models with parameter tuning may be equally efficient for the overall kinetics.

The article evaluates the contribution of different factors in controlling the thermal regime and the heat house-keeping. Despite a sharp increase in suspension viscosity, the overall heat transfer is only slightly affected because of the reaction volume shrinkage. The heat removed by monomer condensation may be more important. A cascade PID controller can keep the dynamic heat balance within 1%. The simulation can predict quantitatively the effect of temperature regime of the molecular weight distribution. The presented modelling offers a rational basis for recipe development and for operation optimisation.

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Fig. 3 - Gel effect and polymer radicals

Fig. 4 - Monomer balance

Fig. 5 -Heat transfer characteristics

Fig. 6 - Dynamic heat balance

Fig. 7 - Temperature control

Fig. 8 - Instantaneous MWD