

## Model Based Operation of Emulsion Polymerization Reactors with Evaporative Cooling: Application to Vinyl Acetate Homopolymerization

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### Abstract

In this work, a dynamic model of emulsion polymerization processes is extended by the inclusion of vaporization from the liquid phases in the reactor to the gaseous phase. The multi-component gas-liquid mass transfer phenomenon is described by a set of algebraic equations which are solved by an iterative procedure. The vaporization fluxes are described by Maxwell-Stefan's diffusion equations. Based upon the extended model, a novel operation strategy is developed. By controlled vaporization, additional heat is removed from the reaction system. This makes it possible to extend the restrictions imposed by the limited heat removal by the cooling jacket considerably. Simulation results are presented for the homopolymerization of vinyl acetate in an industrial scale reactor operated in semi-batch mode. The results show that a significant amount of heat can be removed by evaporative cooling.

**Keywords:** emulsion polymerization; vaporization; modelling; operation; control

### 1. Introduction

Emulsion polymerization is an important multiphase process for the production of a wide range of polymeric materials. The polymerization proceeds as a classical double bond addition reaction initiated via a free-radical mechanism. The reaction is highly exothermic in nature and therefore industrial reactors are often operated under starved conditions. This is due to the limited heat removal capacity of the jackets.

In this paper, we investigate the emulsion polymerization of vinyl acetate, taking into consideration the affect of vaporization of the different species from the liquid phase to the gaseous phase. Since the vaporization reduces the heat content of the reacting medium, it has been termed evaporative cooling. The reaction is carried out at temperatures less than the boiling temperature of the liquid in order to avoid bubbling. The vaporization fluxes are computed by the product of the mass transfer coefficients

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and the concentration gradients in the two phases. The mass transfer coefficients (which are functions of concentrations) are estimated by solving the multicomponent Maxwell-Stefan diffusion equations and by the application of film theory. An algorithm based on the approaches by Burghardt (1983 and 1984) has been developed for this purpose. The model developed here is an extension of our earlier approach, Arora and Gesthusien (2004), where we formulated and analyzed the evaporative cooling model for emulsion polymerization processes. The aim of this paper is to present a model based operation strategy in order to exploit the vaporization phenomenon for the extraction of additional heat out of the system. Further, this approach can be extended to other highly exothermic processes (esp. involving highly viscous systems), where the overall heat transfer coefficient is low, leading to inefficient cooling by the reactor jacket.

## 2. Model Development

Modelling of emulsion polymerization processes has been extensively researched in recent years. Since the process is quite complex and requires complex models, it is beyond the scope of this paper to discuss the various approaches used for modelling of emulsion polymerization process in detail. Only the main equations are described here. The process diagram for which the model is developed is shown in Figure 1.

### 2.1 Emulsion Polymerization Model

Emulsion polymerization is a multiphase process involving primarily three liquid phases (the monomer or droplet phase, the water or aqueous phase, and the oil or particle phase). The reaction starts in the water phase where the initiator disintegrates to form free radicals, which then combine with the dissolved monomer in the aqueous phase to form oligomers. These oligomers either precipitate or are trapped by emulsifier micelles to form particles. The polymerization reaction then mostly takes place in the particle phase. The mole balance equations for monomer and for water can be described as:

$$\frac{dM}{dt} = M_{in} - \frac{\bar{n}N_T k_p [M]^p}{N_A} - [R_T]^w V^w k_p [M]^w - \sum N_M^i A^i + M_{rec} \quad (1)$$

$$\frac{dW}{dt} = W_{in} - \sum N_W^i A^i + W_{rec} \quad (2)$$

where  $\bar{n}$  denotes the average number of radicals per particle,  $N_T$  the total number of particles,  $k_p$  the propagation rate,  $N_A$  Avogadro's number,  $[R_T]^w$  the concentration of oligomers in the water phase and  $V^w$  the volume of the water phase.  $\sum N_j^i A^i$  stands for the total amount of vaporization of species  $j$  from phase  $i$ . The subscript  $in$  denotes the feed to the system and  $rec$  denotes the recycle stream from the condenser. The energy balance for the liquid phase in the semi batch reactor is written as:

$$\frac{d}{dt}(\sum n_i c_i p_i T) = (\sum n_i c_i p_i T)_{in} + r \Delta H_{rxn} - (\sum N_j^i A^i) \Delta H_{vap} \quad (3)$$

where  $(\sum n_i c_i p_i T)$  represents the total amount of energy in the reactor,  $r$  the reaction rate,  $\Delta H_{rxn}$  the enthalpy of reaction and  $\Delta H_{vap}$  is the enthalpy of vaporization.

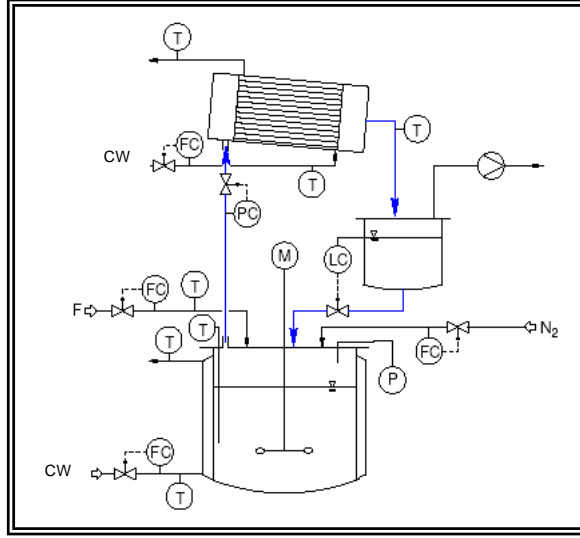


Figure 1. Process diagram

## 2.2 Evaporative Cooling Model

The extension of the emulsion polymerization model is performed by the inclusion of the gas phase. Nitrogen is used as an inert gas for manipulation of the gas phase concentrations. The dynamics of the gas-liquid mass transfer is considered by estimating the vaporization fluxes from the three liquid phases (droplet, water and particle). The vaporization fluxes are described as:

$$(N) = \frac{c}{l} [A_{av}]^{-1} \Xi (y_0 - y_\delta) \quad (4)$$

$$\Xi = \frac{1}{2} \Phi \frac{\exp \Phi + 1}{\exp \Phi - 1}, \text{ where } \Phi = \ln \frac{y_{n\delta}}{y_{n0}} = \sum_{i=1}^{n-1} \frac{N_i k_i}{c_i \tilde{D}_i / l} \quad (5)$$

Here,  $(N)$  is the column vector of vaporization fluxes.  $(y_0 - y_\delta)$  is the column vector of difference of mole fractions in the bulk and interfacial conditions in gas phase.  $[A]$  denotes the inverse diffusivity matrix,  $c_i$  the overall concentration and  $l$  the film thickness. The subscript  $n$  denotes the inert component which is nitrogen.  $\Xi$  denotes the nonlinear Bootstrap relation (that makes the flux of nitrogen equal to zero), which is

a function of existing film and bulk conditions. It is calculated based on the approaches by Burghardt (1983 and 1984) and by Taylor and Krishna (1993). The gas phase component mass balance equations are derived considering the vaporization from the liquid phase and the flow of the gas from the vapour phase to the condenser.

The above equations are explicit in nature and require no iterations if the interface compositions are known. It is assumed that there exists thermodynamic vapour-liquid equilibrium at the liquid side of the interface. Thus, the determination of the gas interface composition, which satisfies the two conditions (vapour liquid equilibrium and flux of inert component being zero) based on the existing conditions of temperature, pressure and compositions in the bulk phases is the key to the solution. An algorithm is proposed (Table 1) that uses an iterative procedure to find the interface composition and thus the overall fluxes.

### 2.3 Operation Strategy

The basic idea is to regulate the concentration of the vaporizing species in the gas phase to a setpoint value. If this set point value is below the thermodynamic equilibrium, then vaporization will take place. The farther the setpoint is away from the equilibrium point the greater is the vaporization flux. This property can be exploited here using the nitrogen flow as a manipulated variable for altering the gas phase compositions. Two independent decoupled feedback loops are constructed to implement the above idea. The first loop controls the pressure in the reactor by regulating the outflow, whereas the second loop maintains a desired mole fraction of water in the gas phase by regulating the inflow of nitrogen. Both controllers are PI-controllers.

*Table 1. Algorithm for the calculation of vaporization fluxes when interface compositions are unknown*

Given	$(x_0), (y_0), P, [\tilde{D}]$
Step 1	Assume $x_\delta = x_0$ for the liquid interface
Step 2	Calculate $y_\delta$ , by estimating interface temperature
Step 3	Compute $y_{avg}$ and calculate $[A_{av}]$
Step 4	Compute $\Phi$ , using the values of step 1 and step 2
Step 5	Compute $\Xi$ (non linear bootstrap coefficient)
Step 6	Calculate $(N)$ (initial guess of flux)
Step 7	Recalculate $\Phi$ (using calculated molar fluxes)
Step 8	Recalculate $y_\delta$ using $\Phi$ from step 7
Step 9	Check for convergence of $y_\delta$ and calculate $(N)$ when converged, else return to step 2

### 3. Results and Discussion

A seeded emulsion polymerization reaction was simulated for an industrial scale reactor in semi batch mode. The vinyl acetate emulsion polymerization model was tested with experimental and simulation results of Sayer et al. (2002). The simulation results are shown in Figure 2 (subfigures A-F). The reaction rate increases in the beginning and then remains almost constant during the whole reaction profile, see subfigure A. This is typical for semi batch reactors where a constant feed rate is used. The reaction starts slowly, thus accumulating some amount of monomer, which then leads to a peak in its concentration (and also in the reaction rate). Instantaneous and global conversion curves are drawn in subfigure B. The initial dip in instantaneous conversion can also be explained by the same argument as the accumulation of monomer in the initial phase of the reaction.

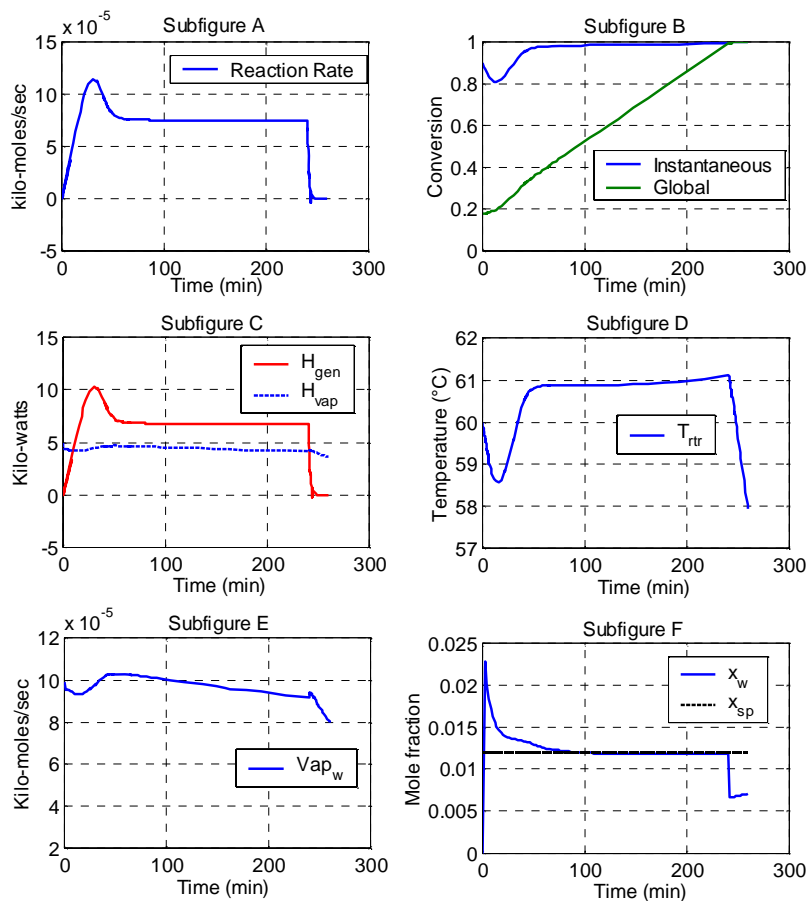


Figure 2. Simulation results for 1000 litre reactor

The rates of heat generation and removal by evaporative cooling are shown in subfigure C. It can be noticed that a significant amount of heat is taken out of the system by the proper usage of the vaporization phenomenon. The simulations clearly show the

advantage of evaporative cooling in addition to the jacket cooling which is limited for highly viscous systems and for large reactors that have relatively small heat transfer areas.

The temperature of the reacting mixture is maintained around 60 °C and the pressure is kept at 1 atmosphere. The vaporization rate for water is shown in subfigure E. It is observed that vaporization flux is strongly dependent on the temperature. As soon as the reaction is over, the vaporization causes the temperature to fall thus leading to its sharp decline.

Since the mole fraction of vinyl acetate is very low in the gas phase due to the high rate of reaction, it was not considered in the control strategy. The value of set point (mole fraction of water in the gas phase) was chosen based on economic considerations (depending on the usage of nitrogen and increment in vaporization flux) of the reaction. Simulation runs were performed for that purpose. The set point along with the actual mole fraction of water in the gas phase is plotted in subfigure F.

#### **4. Conclusions and Future Perspective**

Emulsion polymerization process offer great challenges with respect to industrial operation, optimization and control. Since the reaction is highly exothermic, the process operation is often restricted by the heat removal constraint. One of the major issues is to run the process at safe conditions but at higher reaction rates. Evaporative cooling can be used for this purpose. A model has been developed here that describes the effects of vaporization on the process conditions. The exact estimation of the molar fluxes requires knowledge of the mass transfer coefficients and the interfacial composition, area and temperature. The approach used in this work is based on Burghardt's approach. Since Burghardt's solution can be applied only when the interface and bulk compositions are known, the vapor-liquid equilibrium calculations together with diffusion equations are solved by an iterative procedure.

This model was used to determine the operating set point. Two decoupled control loops are implemented to take advantage of the vaporization phenomenon. The simulation results clearly indicate the advantages of using evaporative cooling over the usual jacket cooling, which is restricted in highly viscous systems and in big reactors (due to the lower heat surface area to volume ratio). In the future, we plan to validate and to improve the results by the experiments.

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