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THE DYNAMIC PID CONTROLLER – STYRENE SUSPENSION POLYMERIZATION REACTOR. TUNING CONTROLLER PARAMETERS

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There is a vast literature available concerning suspension polymerization studies, the corresponding drop size distribution and the tuning of the associated PID controller. However, to the best of the authors' knowledge, there is no study that shows how the functioning of the controller is affected by the drop size distribution, on one hand, and by the polymer content of the suspension, on the other hand. This paper aims at trying to elucidate these aspects, at least partially.

Keywords: suspension polymerization, styrene, PID controller, drop size, organic phase content

1. Introduction

Polymerization is known to be a highly exothermic process, and styrene polymerization is no exception, having an enthalpy of reaction in the order of tens of kJs per mole of transformed monomer [1]. This high generated heat flow should be properly removed, in order for the working temperature to be maintained as close as possible to its desired value, and, consequently, in order for the process to yield a polymer with the expected characteristics.

From this point of view, carrying out this reaction in a liquid-liquid dispersed environment, with water as the continuous phase, clearly presents a strong advantage as compared to the bulk processes. Suspension polymerization is characterized by a topo-chemistry very similar to the bulk process, since the polymerization occurs inside the monomer drops. The continuous phase acts like a heat carrier, removing the heat of reaction developed in the dispersed phase and transferring it, through the reactor wall, to the thermal agent. A good carrier should have low viscosity and high thermal conductivity and this is why water is the continuous phase of choice.

Styrene suspension polymerization is usually carried out in a stirred discontinuous reactor, provided with a heat transfer device, such as a jacket or an external coil, through which the thermal agent flows. The latter should ensure the

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appropriate heat flow from the polymerization medium and thus the designated reaction temperature. Since the suspension polymerization process is discontinuous, the amount of heat which should be removed changes in time, and consequently the flow characteristics of the thermal agent should be appropriately adjusted. Thus, a proper controller should be implemented, to manipulate either the thermal agent flowrate, or its inlet temperature. Even so, thermal runaway cases have been reported for the suspension polymerization processes [2-4], mostly given by stirrer failure or inadequate flowrate and/or temperature of the cooling agent. These runaways advocate the necessity of adequate parameter tuning for the implemented controller.

Controllers can be classified according to the way they respond to the deviation (the error, ε) of the process variable (PV) from its set-point (SP) value, modifying a manipulated variable (MV) to bring PV back to the SP (see Table 1). The simplest is the proportional controller (P), which modifies MV (flowrate of the thermal agent or its inlet temperature) with a value proportional to this error. When the history of the system is important, i.e., when there is a steady drift of the error, the profile of the PV should be integrated with respect to time and divided by the time constant of the process, and MV modified accordingly. This is the integral controller (I). The derivative of the error, forecasting the evolution of the PV in the near future, may be taken into account, changing the MV proportionally to this derivative; this is the derivative controller (D). It should be emphasized that the derivative controller response is heavily influenced by the measurement noise.

These types are not usually used on their own, since their combined actions ensure better performances; however, the presence of the derivative part is useless for systems with constant errors, and thus with zero derivative [5].

The suspension polymerization processes are characterized by drop distributions which depend upon the operating conditions: stirring rate, surfactant concentration, and differences in the physical properties of the drops and of the continuous phase. This study investigates the behaviour of a suspension polymerization reactor provided with a PID controller with fixed parameters; a series of cases are taken into account, consisting in different drop dimensions and different recipes.

Polystyrene beads are produced in large quantities, due to their wide use in day-to-day life. Therefore, the knowledge of the behaviour of the reactor is essential, since this allows improved performances and thus lower energy consumption and higher quality of the polymer.

In the case of the styrene suspension polymerization reactor, the PV is the temperature of the suspension, T_w, which should be kept at a given SP value, T_{ref}, in order to obtain a polymer with the desired properties, given by molecular mass and weight distributions. As MV, the thermal agent flowrate or inlet temperature represent the common choice, the actuators (one or several valves) being of incremental type and with sufficient precision to ensure a proper adaptation to the command. This study considers the flowrate of the thermal agent as the MV.

Table 1

Basic controller expressions

Controller type	Equation
ε	$\varepsilon = \underbrace{T_w}_{PV} - \underbrace{T_{ref}}_{SP}$
P	$P = K_P \cdot \varepsilon$
I	$I = \frac{1}{\tau_i}\int_0^t \varepsilon dt$
D	$D = \tau_d \frac{d\varepsilon}{dt}$

The PID controller is used especially for its versatility and robustness [6-8], the former as a consequence of the derivative component, while the latter is due to the integral part.

2. Model equations

Polymerization, which takes place in a mechanically-agitated cylindrical reactor, cooled by water fed at a fixed temperature and flowing through the jacket, has been considered to observe the kinetic scheme described in [6]. The following assumptions are supposed to be valid in model development:

a) Initiation takes place by peroxide initiator decomposition and, above 90 °C, by self-initiation of the monomer, with third-order kinetics with respect to the monomer. The total initiation rate is computed as the sum of the two individual rates.
b) The termination reaction takes place by recombination.
c) The chain transfer reaction takes place with the monomer molecules.
d) Active centres obey the quasi-steady-state assumption.
e) All the reactions take place in the suspended drops.
f) Drops are isotropic.
g) Diffusion is the only mechanism acting inside the drops.
h) The geometry of the reactor is cylindrical, that of the jacket is annular.
i) The physical properties of the suspension change with conversion and particle distribution.
j) The reaction volume varies with the polymer-monomer fraction.

k) Suspended drops and particles are of spherical shape.

l) The suspended drops have equal volumes.

2.1. Reaction kinetics

The rates of reaction correspond to the stoichiometric equations, except for the monomer self-initiation reaction which obeys assumption a). Rate constants are presented in [6].

2.2. Mass and heat balance equations

Given assumptions e), g), and k), the balance equations have been written in spherical coordinates, and mass and heat were allowed to accumulate inside the suspended drops. The complete mathematical description is given in [9].

Since the polymerization process develops entirely in the discontinuous phase, temperature is the only state variable changing for the continuous medium, which acts as a carrier. The heat balance for water reads:

$$\frac{dT_w}{dt} = \frac{Q_{td} - Q_{tta}}{m_W \; Cp_W} \tag{1}$$

In equation (1), Q_{td} represents the rate of heat transfer from drops through their interface, while Q_{tta} stands for the rate of heat transfer to the thermal agent. The heat flow through the drop-water interface depends on drop surface and on the temperature gradient between the latter and the continuous medium:

$$Q_{td} = 4 \, \pi \, R_{drop}^2 \, N_{drop} \, k_T \, \left(T_{ds} - T_w\right) \tag{2}$$

On the other hand, the cooling agent flowing through the jacket removes heat from the continuous medium inside the reactor – equation (3). The rate of heat transfer to the thermal agent depends on:

- the overall heat transfer coefficient – and thus on the hydrodynamic conditions both inside and outside the reactor and, also, on the physical properties (mean densities, mean heat capacities, mean viscosities) of the fluids on both sides of the jacket;
- the heat transfer area of the reactor (the wetted wall surrounded by the jacket);
- the thermal driving force, temperature difference between the cooling agent and the suspension inside the reactor).

The computations of the average heat transfer properties and hydrodynamic conditions were performed according to [6], [10] and [11].

$$\begin{aligned} Q_{tta} &= K \, \pi \, d_r \left(h_r + \frac{d_r}{4}\right) \left(T_w - T_{aa}\right) = \\ &= D_{ma} \, \frac{Cp_W\left(T_w\right) + Cp_W\left(T_{ai}\right)}{2} \, \left(T_w - T_{ai}\right) \end{aligned} \tag{3}$$

2.3. Tuning of the PID controller

The relation for the PID controller is represented by equation (4). The tuning was performed by the fitting of the temperature profile, with respect to the set point value, the algorithm and solution strategy for which are to be presented in a future paper.

$$PID = K_r \left(T_w - T_{ref} \right) + \frac{\int_0^t \left(T_w - T_{ref} \right) dt}{\tau_i} + \tau_d \frac{dT_w}{dt} \tag{4}$$

$$\tau_T = \frac{4 \pi R_{drop}^2}{D_T} = \frac{4 \pi R_{drop}^2 \rho_S Cp_S}{\lambda_S} \tag{5}$$

The initial values for the constants in the controller are shown in Table 2. The time constant for the integral term was defined with respect to the drop time constant – equation (5). The latter represents the time needed for the heat, generated within the drop, to be transferred to the drop-water interface, and consequently depends on drop size.

Table 2

PID constants

PID constant	Symbol	Value	Units
Proportionality constant	K_r	10	kg/(sec K)
Integral time constant	τi	$0.1\tau_T$	sec
Derivative time constant	τ_d	0.5	sec

3. Results and discussions

3.1. The influence of the drop size on the PID controlled polymerization reactor

In order to show how the drop size affects the performance of the PID controlled polymerization reactor, several runs have been made considering that the dispersed phase is formed of:

a) drops of 0.5 mm in diameter,
b) drops of 2 mm in diameter,

for a suspension polymerization carried out at 30 wt% organic phase.

The resulted PV profiles are displayed in Fig. 1. The small-drop case shows temperature variations within the first 2.5 hours from the reaction start-up. The temperature profile of the continuous medium closely follows the average temperature inside the 0.5 mm drops.

The large-drop case presents a different behaviour. The average temperature inside the drops is about half a degree higher than that of the continuous medium, reaching its highest value after only two minutes, due to the imbalance between the generated and transferred heat flows. After the PID controller proper response, the average temperature of the drops decreases until the transferred and the generated heat flows become equal again. After these 15 minutes of adjustment, the PID controller takes over, being capable of flattening the profile of the average temperature inside drops. Nonetheless, its profile is smoother as compared to the small-drop profile (Fig. 1). The water temperature follows the profile of the average temperature inside the drops, eventually reaching the values obtained for the small-drop case. The gap between the water and organic phase temperatures is significantly larger than in the previous case.

After 4 hours of reaction, the temperature profiles for the two runs overlap, but then split apart for the last third of the process time; the cooling of the large-drop suspension is slower, although, as shown in Fig. 2, the flowrate of the cooling agent is at its minimum for both cases during this time. The reason for this behaviour is the higher thermal inertia of the larger drops.

The same cause leads also to a smooth profile of the MV in time for the system containing large drops. When the monomer concentration is high (i.e., at the beginning of the process), a large amount of heat is generated inside all the drops. The continuous phase removes only a part of it but its temperature has to be levelled by the thermal agent; the PID controller responds by increasing the flowrate of the thermal agent, which rises to its maximum value (Fig. 2). Then, as both the initiator and monomer get progressively consumed, the monomer consumption rate decreases. As a consequence, the generated heat drops too; the transferred heat therefore gets higher than the generated heat, so the temperature of the suspension starts decreasing. Thus, the PID controller gradually adjusts the MV until its minimum is reached (Fig. 2).

In the case of the small drops, although the same amounts of monomer and water are used in both runs, the profile for the MV shows significant sudden variations; given the smaller drop radius, the total drop-water interfacial area is higher and so is the partial heat transfer coefficient from the drop to the continuous medium. Consequently, the generated heat is transferred more quickly to the continuous medium, causing its temperature to increase and forcing the PID controller to adjust the flowrate of the thermal agent to a higher value. The reactor content is then cooled faster than the reaction heat is generated and the PID controller has to diminish the flowrate of the thermal agent. The transferred heat rate becomes again smaller than the generated heat rate and this cyclic evolution leads to the sudden flowrate variations observed in Fig. 2 for the small-drop run.

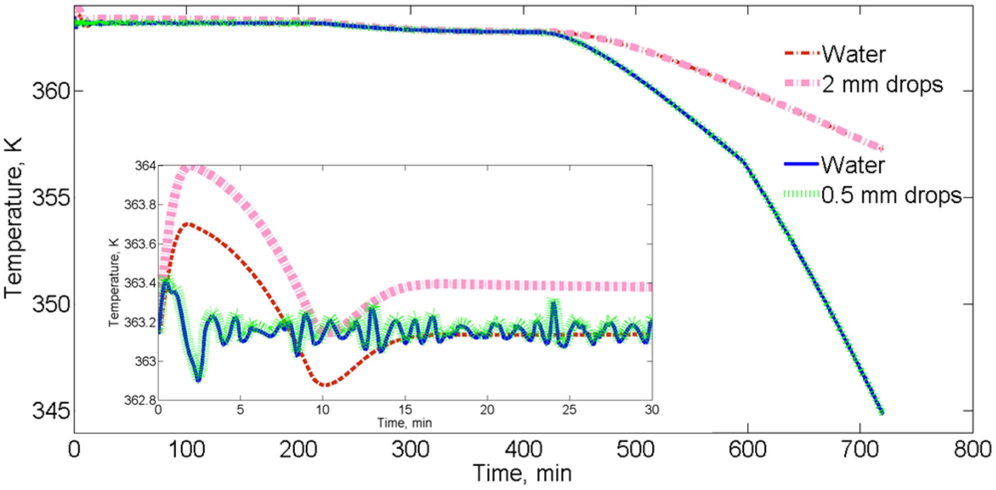

Fig. 1. PV profiles for the small- and large-drop cases, respectively, at 30 wt% organic phase content.

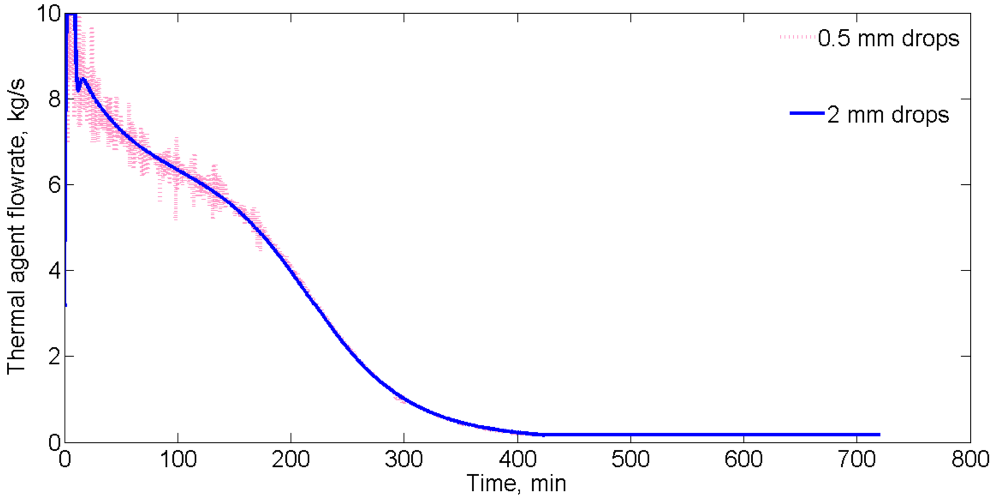

Fig. 2. MV variations for the small- and large-drop runs, respectively, at 30 wt% organic phase content.

3.2. The influence of the initial monomer/water ratio on the PID controlled polymerization reactor

The second objective of this work was to see the influence of the monomer-to-water ratio on the PID controlled polymerization reactor; this ratio was modified by keeping the monomer mass constant and increasing the mass of water. As consequences, the total mass of the system is also modified, together with the heat transfer area between the suspension and the thermal agent, since the radius of the reactor remains unchanged; still, the internal heat transfer area between the drops and water remains the same.

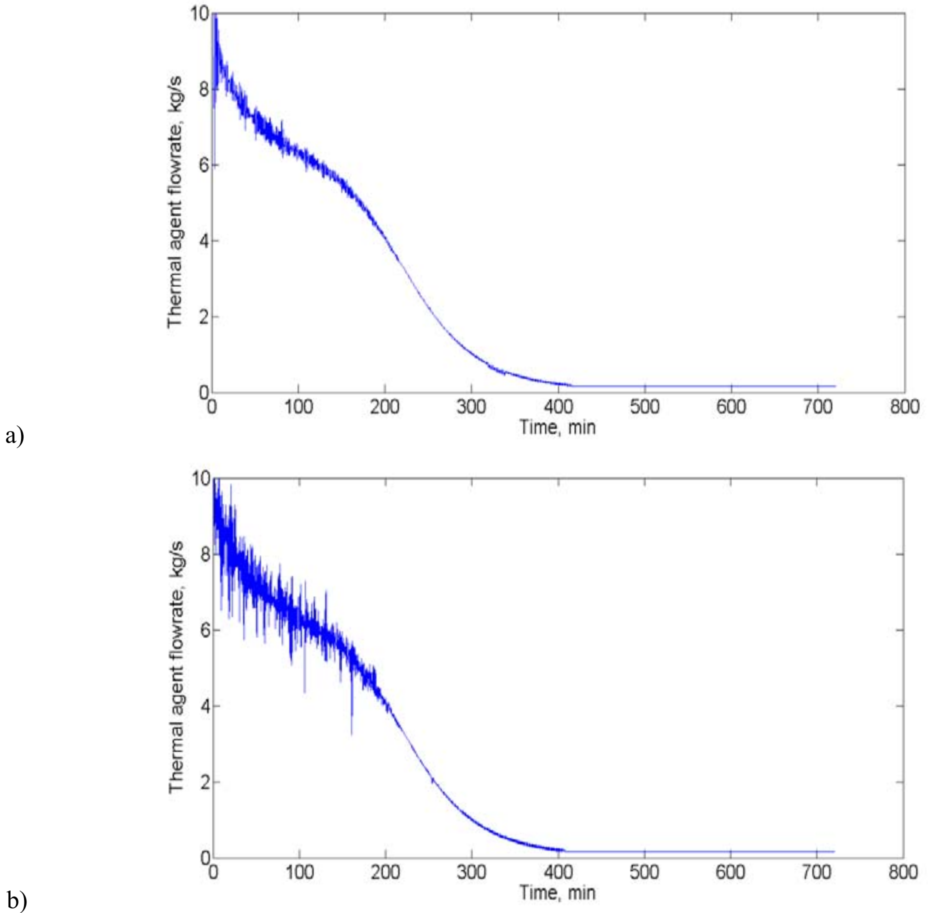

Fig. 3. Profiles of the MV for the 0.5 mm drop suspension, at: a) 25 wt% and b) 50 wt% organic phase content, respectively (for the 30 wt% case, see Fig. 2).

Simulations were ran considering a suspension content of 25, 30, and 50 wt% organic phase, respectively, and the resulted MV profiles are shown in Fig. 3 for 0.5 mm drops. The continuous medium acts like a thermal buffer for the heat generated during the polymerization reaction occurring in the drops. As the organic phase fraction increases, this buffer becomes less and less capable of following the drop temperature variations. Therefore, the thermal agent profile presents sudden changes that become stiffer and of higher amplitude as the monomer fraction in the suspension increases.

The influence of the monomer-to-water mass fraction upon the reaction temperature is depicted in Fig. 4. In order to quantify the effect of changing the initial mass fraction of the monomer phase, we use the concept of generated entropy of a parametric function [12]. Accordingly, the temperature profile of the 0.5 mm drop suspension with 30 wt% organic phase content was taken as the base case for the computation of the cumulative generated entropy with respect to the 25 wt% and 50 wt% organic phase content. The time interval characterized by the most pronounced exothermal effects within the drops (the first 30 minutes) is shown to suddenly generate large differences between the temperatures of the three suspensions, and consequently high values of the cumulative generated entropy; moreover, the differences are more pronounced for the concentrated suspension, because the continuous medium is in this case less available for complete removal of the drops heat. The cumulative generated entropy profiles then show an increase of almost 50% within the next 4.5 hours, meaning that temperature differences between the three suspensions still exist. An almost flat profile of the cumulative generated entropy values follows, indicating that the three suspensions behave similarly until the end of the process.

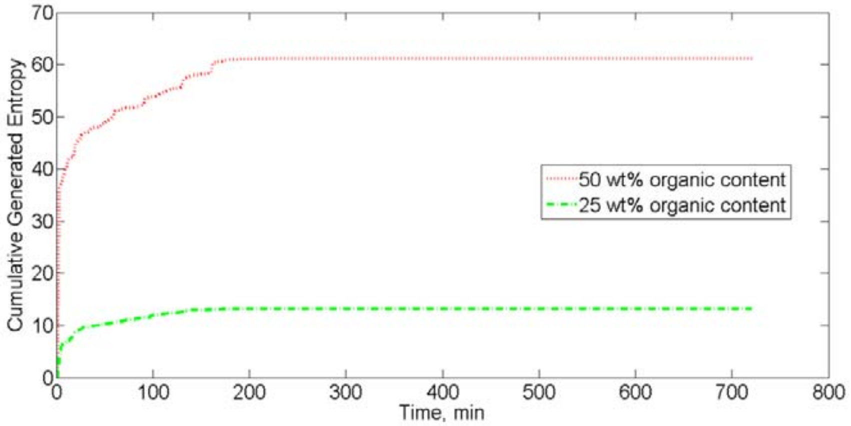

Fig. 4. Mean generated entropy profiles of 0.5 mm drop suspensions for the 50 wt% and 25 wt% organic phase cases with respect to the base case (30 wt% organic phase content).

6. Conclusions

This work has shown the comparative evaluation of the performance of a PID controller, for polymerizing suspensions containing differently-sized drops and a range of ratios of organic versus water phases, respectively. The large-drop run shows smoother profiles of both the MV and the PV, while these variables are characterized by sudden and quick variations in amplitude and period in the case of a small-drop suspension. Moreover, this study has also underlined the different profiles of the MV and PV, respectively, for three polymerization cases where the suspension contained different ratios of organic to water phases. To measure the effects of the monomer-water ratio upon the process, the metric used was the generated entropy of a parametric function. The most unstable profiles of both MV and PV were obtained in the case of the concentrated 0.5 mm drop suspension (50 wt% organic phase content); this means that, when the reaction is to be carried out in these conditions, special attention should be paid to the tuning of the PID controller.

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Notations list

Cp_S	Heat capacity of styrene, J/(kg K)
Cp_W	Heat capacity of water, J/(kg K)
D_{ma}	Mass flowrate of the heat transfer agent, kg/sec
d_r	Reactor diameter, m
D_T	Thermal diffusivity, m^2/sec
h_r	Reactor height, m
K	Overall heat transfer coefficient, W/(m^2 K)
K_r	Proportionality constant of the P, PI and PID controllers, kg/(sec K)
k_T	Drop boundary layer heat transfer coefficient, W/(m^2 K)
m_W	Mass of water, kg
N_{drop}	Number of drops
PID	Adjustment in thermal agent flowrate, kg/sec
Q_{td}	Rate of heat transfer from the drops to the continuous medium, W
Q_{tta}	Rate of heat transfer from the reactor to the thermal agent, W
R_{drop}	Drop radius, m^2
T_{aa}	Average temperature of the heat transfer agent, K
T_{ai}	Inlet temperature of the thermal agent, K
T_{ds}	Temperature on the drop surface, K
T_{ref}	Reference temperature, K, for the adjustment of the thermal agent flowrate
T_w	Temperature of the continuous medium, K
λ_S	Thermal conductivity of styrene, W/(m K)
ρ_S	Styrene density, kg/m^3

τ_d	Time constant, sec, for the derivative term of the PID controller
τ_i	Time constant, sec, for the integral term of the PI and PID controllers
τ_T	Drop time constant, sec

R E F E R E N C E S

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