Rendering Population Balance Solving Strategy Simpler using Size Distribution Function Approximation for Drops/Particles’ Distribution

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The dispersed-phase processes, such as heterogeneous polymerization and crystallization, are widely discussed contexts for application of the population balance. This technique allows, through its parameters, to quantify the changes in dispersed phase size. These coefficients are the rates of occurrence of dispersed phase size-changing phenomena, which, for suspension polymerization, are identified as breakage and coalescence. Based on experimental data, these are estimated in this work, together with the parameters of drop size distribution, in a novel framework assuming time-dependent asymptotic behaviour for the latter.

Keywords: suspension polymerization, drop size distribution, population balance, dynamics, distribution density

The population balance (PB) concept can be applied to any group of distinguishable entities, and assumes the existence of a set of transforming operators acting upon individuals, thus changing them eventually. This paradigm encompasses methods to capture the evolution of populations constituted from multiple distinct members, with respect to some representative external and internal coordinates. The former could be time and/or space, while the latter may include size, concentration, age, or any other property segregating the individuals. As its name suggests it, the PB quantifies the changes in the number of individuals in a given category, together with their characteristics in the domains of interest [1]. In the case of batch suspension polymerization (BSP), these changes are given by coalescence and breakage of drops/particles, with effects on the entities’ size.

Both breakage and coalescence are promoted by stirring, which is essential for avoiding phase separation in a heterogeneous process. Being entrained by the fluid turbulences thus created, there is a large probability that the drops encounter obstacles in their way – the reactor walls, the impeller, reactor baffles, other suspended drops, and so on – and break upon impact. Breakage could also happen due to local shear forces, in the case of large drops. Nevertheless, it is also likely to lead to coalescence. Since new drops are formed from the old ones due to these two processes, both breakage and coalescence should be understood as phenomena leading to “birth” and “death” of particles of a given size, at the same time. eq. (1) expresses the PB for BSP [2].

\[
\frac{d\varphi(v)}{dt} = \frac{1}{2} \left( k_b(u,v) \varphi(v-u) \varphi(u) du - \varphi(v) \int k_c(v,u) \varphi(u) du - k_b(v) \varphi(v) - \beta(v) k_l(v) \varphi(v) \right)
\]  

(1)

where the left hand side (LHS) represents the accumulation rate of the number density \( \varphi \) of the drops of volume \( v \), while the right hand side (RHS) details the processes affecting it: birth and death terms due to breakage and coalescence. The first of them represents the gain of drops of volume \( v \) by the coalescence of a drop of volume \( u < v \) with a drop of volume \( v-u \), at a rate given by the coalescence kernel \( k_c \); since this gain occurs at the expense of two drops, the integral is multiplied by 1/2, according to conservation laws. The second term in the RHS accounts for the disappearance of drops of size \( v \) by coalescence with particles of any volume \( u \). The third term captures the loss of drops of volume \( v \) by breakage; since in this process no other drops are necessarily involved, this term only depends on the probability of existence of drops in this category and on the breakage kernel \( k_b \). Finally, the gain of particles of volume \( v \) may also take place through the breakage of any drops of volume \( u > v \); the breaking drop \( u \) forms \( \beta \geq 2 \) daughter drops. The coalescence and breakage kernels are kinetic terms, expressed according to the mechanisms used to model these phenomena. The subject is widely treated in a series of other contributions [1-4].

The integro-differential form of the PBE represents a source of difficulties in finding its solution. A multitude of methods have been developed in order to yield the best approximation. The most important of these can be classified in the following groups: methods of weighed residuals, methods of moments, discretization methods, and Monte Carlo methods. Their description can be found in Ramkrishna’s work [1]. Costa et al. [5] also present a state of the art review for some of them. There are also methods that do not respect the principles of any of these groups, and are considered as alternatives; such examples are the parallel parent and daughter drop classes method [6], the drop test method [7], the maximum entropy method [8], and the decomposition of kinetics [9].

In spite of the multitude of existing methods, they are all computationally expensive and thus very hard to integrate in reactor modelling for obtaining a complete image on the process. The present work is therefore intended to offer an alternative, by approximating the distribution function to a known form and defining its parameters in relation to time. The experimental set-up and results will be described, followed by the proposed model. The modelling results will be shown and discussed, allowing for the conclusions to be drawn.

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Experimental part

Materials and methods

The monomer (methyl methacrylate – MMA), provided by Sigma Aldrich, of 99 % purity, was distilled to remove the inhibitor (30 ppm). Benzoyl peroxide, 99.1 % pure, supplied by Fluka, was used as an initiator, in a proportion of 3 g / 100 mL MMA, subsequent to being recrystallized; a corresponding quantity was premixed with 25 mL of monomer and the solution was poured in 100 mL of water, under continuous stirring, in a 250 mL three-necked round-bottomed flask. The temperature was maintained at 70 °C by a water bath with a thermostat, for 2 h; it was then raised to 75 °C for the 30 min and finally to 80 °C for the last half an hour, in order for the initiator to be completely consumed. The experiment was designed to take place at 480 rotations per minute. Samples were taken along the entire process, at fixed intervals, and placed on glass plates, where they were let to dry.

The samples were visualized with a MOTIC Image Plus, version 2.0 ML, optical microscope with a magnifying capacity of 10x and a MOTICAM 1000 digital camera attached (both from Motic™), that was used in photographing the samples. The obtained images – fig. 1 for an example – were analysed with SigmaScan Pro 5 (Systat Software), which measured the shape factor, diameter, area and volume of each visualized drop. Since of these, only the volumes are additive during the breakage-coalescence phenomena, they were chosen to represent the characteristic dimension of the drops.

Data processing

Given the large range of drop volumes obtained from measurements (from a few tens up to hundreds of thousands of cubic microns), a semi-logarithmic graphical representation was chosen for the density of the distribution. The logarithms of drop volumes were calculated and the results were normalised using equation (2), where \( v \) is drop volume.

\[
x = \frac{\lg(v)}{\lg(\max(v))}
\]

This procedure implied finding the highest drop volume from all the samples, over the entire time span (180 min) of the chemical process. As a consequence to this approach, the drops/particles were redistributed on a dimensionless scale from 0 to 1, improving the clarity of the representation of the experimental results.

It should be noted that, while the measurement technique only allows obtaining discretized results, the drops’ volumes can in fact take any value in the continuous range. The volume interval, after being rendered logarithmic, was divided in classes according to the principles of continuous variables representation in descriptive statistics. Then, following the above observation, the drops in each size class were counted and the obtained absolute frequencies were interpolated against the continuous normalised interval, to yield the frequency function \( f(x) \) (the interpolated number of counts of \( x \)). This allows computing the number density of the distribution (the probability) \( \varphi(x) \) – eq. (3) – for values over the entire range.

\[
\varphi(x) = \frac{f(x)}{\int_{\min(x)}^{\max(x)} f(x) \, dx}
\]

The experimental data yielded figures 2 and 3; markers are used here to represent the experimentally obtained values, while the continuous lines have been used only for a clearer representation of the drop size distribution (DSD) shape.

Figure 2 presents the population number density for the samples withdrawn from the reactor within the first hour of the polymerization process. It shows that the distribution shifts in time, while maintaining its shape, from lower to higher average drop size, as a consequence of the increased relative importance of agglomeration over the breakage phenomenon.

This situation arises from the evolution of the polymerization process, accompanied by drastic changes in the physical properties of the drops. At this stage, the concentrated monomer-polymer syrup is highly viscous and neither drop coalescence nor breakage is advantaged. The DSD afterwards preserves shape, mean and variance until the end of the process (fig. 3).
Model development

The PB is a complex framework, not only in what concerns its mathematical expression, but also in choosing the most appropriate method for finding its solution. A complex approach in modelling the BSP process includes determining the physical properties of the dispersed phase, which are in their turn influenced by the instantaneous conversion inside the drops, therefore by reaction rate and, ultimately, by drop temperature. Such a model already has a high degree of complexity and, if it is planned to be used in conjunction with the PBE, the latter should be reduced to as simple a form as possible. The approach proposed below aims at providing a PBE capable of describing, for any moment in time, the DSD of the system under discussion. It is based on complex function development, without, however, pertaining to the existing classes of methods, but rather to the alternative methods group. It starts from the following assumptions:

a) the chemical process is confined to drops so that the monomer does not diffuse through the drop-water interface to dissolve in the continuous phase;

b) the volume variation of the drops due to the polymerization process is neglected.

The drop number distribution function

As figures 2 and 3 show, the distribution shape is preserved throughout the polymerization process, although the values of the DSD parameters change in time. Their examination led to the idea of bimodal normal distribution – eq. (4) – which makes (5) a non-linear equation relating distributions’ parameters to the transforming operators, i.e. coalescence and breakage.

The parameters of the normal distribution are the mean and the variance, defined as the distribution’s first moment – eq. (5) – and second moment with respect to the mean –eq. (6):  

\[
\phi(x,t) = \alpha \frac{\exp \left( \frac{1}{2} \frac{x - \mu_1}{\sigma_1(t)} \right)^2}{\sigma_1(t) \sqrt{2\pi}} + (1-\alpha) \frac{\exp \left( \frac{1}{2} \frac{x - \mu_2}{\sigma_2(t)} \right)^2}{\sigma_2(t) \sqrt{2\pi}}
\]

(4)

The parameters of the normal distribution are expressed in eq. (4).

\[
\mu = \frac{\max(x)}{\min(x)} \int x \phi(x) dx \\
\sigma^2 = \frac{\max(x)}{\min(x)} \int x^2 \phi(x) dx - \mu^2
\]

(5)

(6)

The parameters of the DSD were designed to start from some given initial values \(\mu_{1,0}, \mu_{2,0}, \sigma_{1,0}, \sigma_{2,0}\) corresponding to the initial state of the BSP process. In time, due to the coalescence/breakage phenomena, there is a shift of the distribution towards the final state; it still remains a bimodal normal distribution, but its parameters continuously change. This transformation is quantified by the relationships (7) and (8). The first term guarantees that the distribution starts with an initial, given mean, which in time asymptotically moves towards the final value, as ensured by the second term. In this way, the distribution parameters become increasingly dependent on \(\mu_{1,i}, \sigma_{1,i}, K_{1,i}^c, K_{1,i}^b\)

\[
\mu_i(t) = \mu_{i,0} \exp(-t) + \frac{t \mu_{i,f}}{t + K_{\mu,i}} \\
\sigma_i(t) = \sigma_{i,0} \exp(-t) + \frac{t \sigma_{i,f}}{t + K_{\sigma,i}}
\]

(7)

(8)

This approach has a series of advantages, namely the fact that the DSD is known for any time, and, most important, the simplification of the formerly integro-differential PBE. The relationship (9) shows a form of the latter for the case of binary breakage \((\beta=2)\).

\[
\frac{d\phi(x)}{dt} = k_a \left[ \frac{1}{2} \int \phi(x-y) \phi(y) dy - \phi(x) \right]_{\min(x)}^{\max(x)} + k_b \left[ \frac{\max(x)}{2} \int_{\min(x)}^{\max(x)} \phi(y) dy - \phi(x) \right]
\]

(9)

The differential and integral terms can be computed analytically using the bimodal normal distribution – eq. (4) – which makes (5) a non-linear equation relating distributions’ parameters to the transforming operators, i.e. coalescence and breakage.

The data fitting strategy – finding model’s parameters

Our mathematical model, comprising eq. (4) – (9), was intended to fit the experimental results as closely as possible. This fitting was achievable by finding the optimum model parameters – \(\mu_{1,i}, \sigma_{1,i}, \mu_{2,i}, \sigma_{2,i}, K_{1,i}, K_{2,i}\) and \(\beta\) of the bimodal normal distribution assumed, and the breakage and coalescence kernels \(k_a^b, k_b^c\) from the PBE. As an optimizer, the genetic algorithms were chosen, due to their advantage over deterministic methods [10]; the “ga” built-in function in Matlab™ (MathWorks, Natick, MA), version R2012b, was used to find the values of the first 13 parameters by minimizing the objective function \(FO_{Ob_i}\). The latter – eq. (10) – should include the norm, over the entire time span of the process, of the distances between the experimental density of the DSD \(\phi_{exp}\) and that computed by the relationship (4).

\[
FO_{Ob_1} = \|\phi_{exp}(x,t) - \phi_{calc}(x,t)\|_2
\]

(10)

This, however, does not address the PBE parameters \(k_a^c, k_b^b\). Therefore, the \(FO_{Ob}\) should be supplemented with the distance, for every sampling time, between the rate of change in the experimental distribution density and that predicted by the PB, as shown in the relationship (11). The final form of the objective function is given by eq. (12).

\[
FO_{Ob_2} = \left[ k_a \left[ \frac{1}{2} \int_{\min(t)}^{\max(t)} \phi(x-y,t) \phi(y,t) dy - \phi(x,t) \right]_{\min(t)}^{\max(t)} \right] + k_b \left[ \frac{\max(t)}{2} \int_{\min(t)}^{\max(t)} \phi(y,t) dy - \phi(x,t) \right] - \frac{d\phi_{exp}(x,t)}{dt}
\]

(11)

\[
FO_{Ob} = FO_{Ob_1} + FO_{Ob_2}
\]

(12)

Results and discussions

The optimisation results were used for plotting the computed distribution and comparing the latter with the experimental curve. Figure 4 shows the graphical representations corresponding to 3 samples – in the beginning of the process, in the middle, and at the end. The fitting proves efficient, fact confirmed by the low value of the objective function, in table 1.
The values obtained by minimizing the objective function (12) using genetic algorithms as an optimization technique are also shown in Table 1 for the 15 parameters of the model. While the first mean increases with about 70%, \( \mu_2 \) increases about three times. The high transition coefficients show that these changes happen at a rather slow pace.

However, while the means of the two DSD’s evolve according to the same pattern with respect to each other, the standard deviations show different evolutions. The first distribution becomes narrower in time, and the second one is rather stationary from this point of view. The abrupt evolution in the first case is emphasized by the low value of \( K_1, \sigma \). The second case is shown to suffer a slower narrowing due to a large \( K_2, \sigma \) value.

Concerning the drop dynamics, the values of the coalescence and breakage rates explain the shift of both distributions towards larger drop/particle sizes, with \( k_a \) much higher than \( k_b \).

The partition coefficient \( \alpha \) gives the weight of the first distribution. Its value, above 0.5, shows that the bi-modal distribution is more strongly represented by the group of drops/particles described by \( \mu_1 \) and \( \sigma_1 \). The second group, however, is shown not to have a negligible contribution to the overall evolution of the system, since \( \alpha \) is still quite far from unity.

The model assumption of two convoluted normal distributions may stand for a phenomenon consisting of two mechanisms competing in establishing the final DSD. The fact that in our system a population of larger drops/particles coexists with a population of smaller entities shows the competition between coalescence and breakage. While the latter one is more poorly represented, the smaller drops mainly suffer coalescence and shift towards bigger sizes. Although the second distribution shows more spectacular changes, the drops/particles in both groups tend to become larger, showing once again the predominance of coalescence over breakage.

In order to complete the fitness check, a statistical analysis of the model has been performed, by evaluating, for each sample, the differences between the experiment and the prediction. The sum of squared deviations of the model predicted values from the dependent variable mean (SSR) and sum of squared residuals (SSE) were computed according to relationships (13) and (14), respectively, where \( n \) is the number of experimental points and \( \overline{\phi} \) is the average of the experimental values – eq. (15). Furthermore, the mean of squared deviations (MSR) and the mean of squared residuals (MSE) can be obtained from SSR and SSE.
SSE, respectively, by the use of relationships (16) and (17), where \( p \) is the number of model parameters.

\[
SSR = \sum_{i=1}^{n} (\varphi_{\text{Calc},i} - \bar{\varphi})^2
\]  

\[
SSE = \sum_{i=1}^{n} (\varphi_{\text{Exp},i} - \varphi_{\text{Calc},i})^2
\]  

\[
MSR = \frac{SSR}{p - 1}
\]  

\[
MSE = \frac{SSE}{n - p}
\]  

Based on these results, the F test was performed. F is computed as the ratio between MSR and MSE, which yields the value 153. The Fisher critical value (the quantile calculated for a significance level of 5 % and \( p -1 \) and \( n-p \) degrees of freedom), is 1.73, much smaller than the computed F value, resulting in a high significance of the proposed model.

The values of \( R^2 \) – the correlation between \( \varphi_{\text{Exp}} \) and \( \varphi_{\text{Calc}} \) – were computed and represented graphically against time in figure 5. \( R^2 \) is seen to vary between 0.62 and 0.98, averaging at 0.84; this means that the model is able to explain more than 80 % of the variations that take place during the process. Moreover, parity plots were chosen as a way to visually evaluate the model’s performance in relation to the experimental data. Figure 6 shows the parity plots for the initial sample (taken immediately after the addition of the organic phase) and for the final one. The former case is shown to be characterised by a poor correlation (fig. 5), mainly caused by the random formation of drops as the organic phase was being poured in the reactor, corroborated to a lack of time for coalescence and breakage to occur and to favour a dominant drop size. On the other hand, the last sample is shown by the \( R^2 \) value to be well predicted by the model, and consequently the parity plot also shows good concordance between the experiment and the prediction.

Conclusions

This study was focused on finding the characteristic parameters of a drop population and the way they modify during the suspension polymerization process. A novel approach has been presented, with time-dependent mean and standard deviation. This transforms the integro-differential PBE in a set of non-linear equations, making it simpler to search for the parameters through optimization. The practical experiment targeted the suspension polymerization of methyl methacrylate as a case study. Drop volumes were taken as the internal coordinate of the population balance, prior to rendering them logarithmic and to normalization. Optimization was performed to find the values of the model parameters that would ensure a good fit of the computed number distribution density with the experimental data. The modelling results were found to be in good agreement with the experimentally obtained information, proving the reliability of the approach. Once the parameters of the process are known, the population balance paradigm can be further coupled with the reactor models, for a more realistic simulation of the suspension polymerization process.

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