Achieving Target Emulsion Drop Size Distributions using Population Balance Equation Models of High Pressure Homogenization *

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Abstract: A population balance equation (PBE) model that accounts for drop breakage and coalescence in high pressure homogenization was used for emulsion product design. Six adjustable parameters were estimated by nonlinear optimization from measured drop volume distributions at a specified operating condition. The values of two parameters were estimated at four different homogenization pressures and interpolated to allow improved prediction over a range of pressures. Using two alternative objective functions, the parameterized model was used to determine the pressure of each homogenization pass needed to achieve the target drop size distribution at the final pass. Homogenization experiments performed to validate the model predictions produced measured distributions in very good agreement with two target distributions.

Keywords: Process modeling, population balance equation model, nonlinear parameter estimation, nonlinear optimization, particle size control.

1. INTRODUCTION

Oil-in-water emulsions are ubiquitous dispersed phase systems with diverse applications that include consumer products, processed foods, polishes, waxes, agricultural sprays and road surfacing materials (Becher, 2001; Chappat, 1994; Israelachvili, 1994). In the foods industry, emulsions constitute natural foods as well as numerous processed products such as milk, butter, margarine, ice cream, sauces and desserts. Food emulsions contain edible oils, water and biocompatible surfactants as the major ingredients and vitamins, minerals and/or flavors as minor ingredients (McClements, 2005). Emulsion system formulation and processing operations both impact the drop size distribution, a key property that influences emulsion rheology, stability, texture and appearance. A typical processed food requires the drop size distribution to be maintained within acceptable limits, which includes achieving a prescribed mean drop size, maintaining small variations about the mean and avoiding very small or large drops that adversely affect product properties such as texture and appearance.

Oil-in-water emulsions are typically formed by first preparing a coarse premix using a low shear stator-rotor type device that mixes the various ingredients into a stable form. This premix is then processed with a high shear device in which relatively large drops are broken into much smaller drops. In high pressure homogenization, the coarse emulsion is passed through a small orifice under very high pressure. The fluid stream passes radially through the narrow gap formed between the piston and the valve seat at high velocity, creating a local environment of high turbulence and shear stress that causes drop deformation and breakage. Drop breakage leads to the creation of new interfacial area that must be stabilized by the surfactant. If newly formed drops are not sufficiently covered by surfactant, the drops will coalesce to form larger drops. Under typical industrial conditions where surfactant use is minimized to reduce manufacturing costs, drop coalescence is prevalent due to insufficient free surfactant in solution (Walstra, 1993). While drop breakage under laminar conditions has been extensively studied (Dhingra, 2001; Gupta, 2004), the problem of turbulent breakage and coalescence is less understood.

Due to lack of quantitative understanding, new emulsified products are currently developed by combining a broad knowledge of previous product formulations with empirical scientific experimentation. An alternative to brute force experimentation is to utilize a suitable mathematical model to predict the drop size distribution for different emulsion formulations and processing conditions. The population balance equation (PBE) modeling framework (Ramkrishna, 2000) is particularly well suited for this problem as functions describing drop breakage and coalescence can be incorporated within a fundamental number balance equation to predict the evolution of the drop size distribution. Several investigators have develop-
oped PBE models of high pressure homogenizers (Kelly and Muske, 2004; Soon et al., 2001; Tcholakova et al., 2007; Vankova et al., 2007b,a). With a only a few exceptions (Maguire et al., 2003), these homogenizer models neglect drop coalescence under the assumption that newly formed drops are sufficiently covered by surfactant. As part of our previous work on high pressure homogenization, we have developed breakage-only PBE models for prediction of the drop volume distribution (Raikar et al., 2009, 2010). Through experimental and computational studies, we showed that our model emulsion system exhibited negligible coalescence due to the low oil-to-surfactant ratio (5% oil, 1% surfactant) used. In this paper, we incorporate drop coalescence functions to allow the drop volume distribution to be predicted for a much higher oil-to-surfactant ratio (50% oil, 1% surfactant). Nonlinear optimization is used to estimate six adjustable parameters in the drop breakage and coalescence functions to match measured size distributions. The resulting model is used to develop a methodology for computing the number of homogenizer passes and the operating pressure of each pass such that target emulsion drop size properties are achieved in a least-squares sense.

2. PBE MODEL DEVELOPMENT

2.1 Model Formulation

The PBE is formally derived from a number balance on particles by accounting for the various rate processes such as breakage and coalescence that affect particle size (Ramkrishna, 2000). In this study, a volume structured PBE was used because light scattering most directly measures drop volume. Although homogenizers have distinct zones where local shear forces can change dramatically (Hakansson et al., 2009), we treat the homogenizer as a well-mixed batch system to avoid the complexities associated with including spatial variations. In this case, the PBE can be written as (Raikar et al., 2009; Coulaloglou and Tavlarides, 1977),

$$
\frac{\partial n(v, t)}{\partial t} = -g(v)n(v, t) + \int_0^\infty \beta(v, v')g(v')n(v', t)dv' - n(v, t) \int_0^\infty C(v, v')n(v', t)dv' + \frac{1}{2} \int_0^v C(v-v', v')n(v-v', t)n(v', t)dv'$$

where \( v \) is the volume of the particle; \( n(v, t)dv \) is the number of drops with volume in the range \([v, v + dv]\) per unit volume of dispersion at time \( t \); \( g(v) \) is the breakage rate representing the fraction of drops of volume \( v \) breaking per unit time; \( \beta(v, v') \) is the daughter drop distribution function representing the probability of forming a daughter drop of size \( v \) from breakage of a mother drop of size \( v' \); and \( C(v, v') \) is coalescence frequency representing the rate at which drops of size \( v \) and drops of size \( v' \) coalesce. The model requires specification of the functions that describe the breakage and coalescence processes, namely \( g(v) \), \( \beta(v, v') \) and \( C(v, v') \). The PBE (1) describes the evolution of the number density \( n(v, t) \), while particle size analysis usually provides measurements of the volume percent distribution \( n_p(v, t) \). Under the standard assumption that drops are spherical, the two distributions are easily related (Raikar et al., 2009). The measured volume distribution of the coarse pre-emulsion is used as initial condition for the first homogenizer pass. Each pass corresponds to one dimensionless time unit, and the initial condition for each subsequent pass is the predicted volume distribution from the previous pass.

The PBE (1) contains three functions that must be specified to compute the drop size distribution. Following our previous work (Raikar et al., 2009), the breakage rate \( g(v) \) is assumed to be determined by turbulent breakage of drops by both inertial and viscous forces such that \( g(v) = g_1(v) + g_2(v) \). The first breakage function \( g_1(v) \) is derived assuming drops break due to collision with turbulent eddies (Coulaloglou and Tavlarides, 1977),

$$
g_1(v) = K_1 v^{-2/3} \exp\left(-\frac{K_2 v (1 + \phi)^2}{\rho d v^{9/2} \epsilon^{2/3}}\right)$$

where \( K_1 \) and \( K_2 \) are adjustable constants. The second breakage rate function \( g_2(v) \) is derived assuming that drop breakage results from turbulent shear (Raikar et al., 2009),

$$
g_2(v) = K_3 \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{\rho_d v}{\eta_d}\right)^{1/2} \exp\left(-\frac{K_4 \sigma^2 \lambda}{v^{4/3} \epsilon \rho_c}\right)$$

where \( K_3 \) and \( K_4 \) are the adjustable constants. The two breakage rates depend on the homogenizer pressure \( P \) through the energy dissipation rate \( \epsilon \) (see below) and emulsion properties including the dispersed phase volume fraction \( \phi \), the interfacial tension \( \sigma \), the dispersed phase density \( \rho_d \), the continuous phase viscosity \( \eta_c \) and the dispersed phase viscosity \( \eta_d \) through the ratio \( \lambda = \frac{\eta_d}{\eta_c} \).

We have shown that these dependencies are necessary for the PBE model to be predictive over a range of formulation and homogenization conditions with a single set of constants \( K_1 - K_4 \) (Raikar et al., 2009, 2010).

The breakage rate function is specialized to high-pressure homogenizers by using the following relation for the energy dissipation rate (Vankova et al., 2007b,a),

$$
\epsilon = \frac{\Delta P Q}{V_{diss}}
$$

where \( \Delta P \) is the applied pressure, \( Q \) is the volumetric flow rate and \( V_{diss} \) is the valve gap volume which depends on valve gap distance \( h_{gap} \). Equations for \( V_{diss} \) and \( h_{gap} \) can be found in our previous work (Raikar et al., 2009). As in our previous breakage-only PBE model, we use the power law product form of the generalized Hill-Ng distribution (Hill and Ng, 1996; Zaccone et al., 2007) as the daughter drop distribution function \( \beta(v, v') \) to model the breakage of a mother drop into multiple daughter drops. The parameter \( q \) is chosen as unity to represent the uniform probability of daughter drops of any size \( v < v' \) being formed due to breakage of a mother drop of size \( v' \). In this case, the daughter drop distribution function has the form,

$$
\beta(v, v') = (p - 1) \left(1 - \frac{v}{v'}\right)^{p-2}
$$
where $p \geq 2$ is the number of daughter drops formed from breakage of a single mother drop. Based on preliminary simulation results (not shown), we determined that the best fit of drop volume distribution data was obtained for $p = 80$. While laminar flow experiments have established that a mother drop can break into numerous daughter drops (Zhao and Goveas, 2001), the assumption that turbulent homogenization conditions could produce as many as 80 daughter drops from a single mother drop requires experimental testing beyond the scope of this study.

The coalescence frequency $C(v, v')$ of drops of size $v$ and $v'$ is modeled as the product of the drop collision frequency $h(v, v')$ and the coalescence efficiency $\lambda(v, v')$: $C(v, v') = h(v, v')\lambda(v, v')$. While certainly not mechanistically correct, we follow the common practice of modeling the collision frequency assuming that drops in turbulent flow behave like gas molecules (Coulaloglu and Tavlarides, 1977),

$$h(v, v') = \frac{K_5 v^{1/3}}{1 + v^{2/3} + v'^{2/3}} \left(\frac{v^{2/3} + v'^{2/3}}{v^{2/3} + v'^{2/3}}\right)^{1/2}$$

(6)

where $K_5$ is an adjustable constant. The coalescence efficiency is modeled to depend on the contact time of droplets, with coalescence occurring if the contact time is greater than the time required for the liquid film between two drops to drain (Coulaloglu and Tavlarides, 1977),

$$\lambda(v, v') = \exp \left[ -K_6 \frac{\eta_p \rho_c \varepsilon}{\sigma^2 (1 + \phi)} \left( \frac{v^{1/3} v'^{1/3}}{v^{1/3} + v'^{1/3}} \right)^4 \right]$$

(7)

where $K_6$ is an adjustable constant. Similar to the breakage rate, the coalescence frequency depends on the homogenizer pressure $P$ through the energy dissipation rate $\varepsilon$ and emulsion properties including the continuous phase density $\rho_c$ and $\phi$, $\sigma$ and $\eta_p$.

2.2 Emulsification Experiments

Oil-in-water emulsions were prepared using vegetable oil (Fisher Scientific) as the dispersed phase and water as the continuous phase. Emulsions consisted of 50 wt% oil and 1 wt% Pluronic F-68 surfactant with the remaining water. Emulsions were prepared using a two-step process. First approximately 400 ml of coarse pre-emulsion was prepared by mixing the ingredients in a stator-rotor device (Ultra-Turrax Model T25, Rose Scientific Ltd.) at 16000 rpm for 15 minute. About 100 ml of pre-emulsion was processed in a high-pressure homogenizer (Emulsiflex C-3, Avestin Inc.) to reduce the average drop size. The base case homogenization pressure was chosen as 800 bar to produce small drops likely to undergo coalescence. Multiple passes were performed by reprocessing the emulsion obtained from the previous homogenizer pass. After each pass approximately 2 ml of emulsion was sampled to analyze the drop size distribution. Extensibility experiments were performed at three lower pressures (200, 400 and 600 bar). Drop size distributions were measured using static light scattering ( Mastersizer S, Malvern Instruments). Densities, viscosities and the interfacial tension were measured prior to each homogenization experiment. Continuous and dispersed phase densities were measured using a Bio-Rad 36XMX densitometer. The oil-water interfacial tension $\sigma_{o/w}$ was measured by drop shape analysis (Model DSA-10 Tensiometer, KRUSS Instruments) at 25°C.

2.3 Parameter Estimation and Model Extensibility

The PBE model (1) was solved numerically by approximating the integral expression using the fixed pivot technique (Kumar and Ramkrishna, 1996) with 100 equally spaced node points. The discretized PBE model consisted of 100 nonlinear ordinary differential equations in which the independent variable was time and the dependent variables represented the volume percent distribution at each node point. The ODE system was solved with the Matlab integration code ode45 using the measured premix distribution as the initial condition $n_p(v, 0)$.

The constants $K_1 - K_4$ in the breakage rate function and $K_5 - K_6$ in the coalescence frequency function were estimated from base case homogenization experiments. The data used for parameter estimation were emulsion properties ($\phi$, $\sigma$, $\rho_c$, $\eta_p$, $\eta_w$), the premix volume distribution $n_p(v, 0)$ and the measured drop volume distribution $n_p(v, t)$ after each homogenization pass. The 100 ODEs obtained from spatial discretization of the PBE model were temporally discretized using orthogonal collocation with 15 finite elements and 2 internal collocation points per element to produce a large set of nonlinear algebraic equations. Each homogenizer pass corresponded to 3 finite elements. The algebraic equation system was posed as a set of equality constraints in the nonlinear optimization problem. The least-squares objective function $\Psi$ used for parameter estimation was,

$$\Psi = \sum_{i=1}^{N} \sum_{j=1}^{n} \left[ \frac{|\hat{n}_p(v_j, i) - n_p(v_j, i)|^2}{\sum_{j=1}^{n} |n_p(v_j, i)|^2} \right]$$

(8)

where $n_p(v_j, i)$ is the measured value of the drop volume distribution at drop volume $v_j$ and homogenizer pass $i$, $\hat{n}_p(v_j, i)$ is the corresponding predicted value from the discretized PBE model, $n$ is the total number of spatial node points, and $N$ is the number of passes. The objective function was minimized subject to the large number of equality constraints representing the discretized model equations as well as continuity conditions across the finite elements. The optimization problem was formulated in AMPL (Fourer et al., 2003) and solved using the nonlinear program solver CONOPT (Drud, 1994). Values of the objective function $\Psi$ were used to judge the quality of model predictions for different experiments.

At the base case conditions where parameter estimation was performed, the PBE model produced very accurate predictions of the volume distribution and mean diameter (Figure 1) following each homogenizer pass. Next the model parameters were re-estimated at homogenization pressures different than the base case value to further access predictive capability. The homogenization pressure was incorporated into the model through the energy dissipation rate (4). For each pressure, drop volume distributions measured following five homogenization passes were used to estimate $K_1 - K_6$. As shown in the second column of Table 1, parameter re-estimation yielded very accurate predictions of drop volume distributions at each
pressure. Finally the model parameters estimated at 600 bar were used to predict drop volume distributions at the other three pressures without re-estimation. The results are shown in the third column of Table 1 and Figure 2. Although the model showed good qualitative agreement with data, we found that the predictions were not sufficiently accurate at other pressures to be used for model-based design. Analysis of the estimation results showed that the model parameters $K_2$ and $K_4$ that determine efficiencies of the two breakage mechanisms varied significantly between the four pressures. Therefore, these parameter values were interpolated to generate improved predictions (see below).

Table 1. Minimized objective function values at different pressures

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Estimation at each pressure</th>
<th>Estimation at 600 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.077</td>
<td>1.284</td>
</tr>
<tr>
<td>400</td>
<td>0.074</td>
<td>0.385</td>
</tr>
<tr>
<td>600</td>
<td>0.062</td>
<td>0.632</td>
</tr>
<tr>
<td>800</td>
<td>0.025</td>
<td>0.236</td>
</tr>
<tr>
<td>Total</td>
<td>0.208</td>
<td>1.934</td>
</tr>
</tbody>
</table>

3. MODEL-BASED DESIGN OF HOMOGENIZER OPERATING CONDITIONS

3.1 Optimization Methodology

The PBE model was used to predict homogenization conditions that would achieve the specified emulsion drop size properties. In this study, the product design problem was formulated as a nonlinear least-squares optimization problem with the number of homogenizer passes and the operating pressure at each pass chosen as decision variables. As discussed in the previous section, improved predictions were achieved by interpolating the breakage rate parameters $K_2$ and $K_4$ using values estimated at four pressures that covered the range of interest (Figure 3).

The optimization formulation requires specification of an objective function for achieving the target emulsion drop size properties. We considered two alternative least-squares objectives for this purpose. The first objective represents the drop size distribution in terms of the Sauter mean diameter ($d_{32}$) and the polydispersity ($PD$),
First we considered the problem of achieving a drop size distribution with \(d_{32\text{tar}} = 0.3\) mm and \(PD_{\text{tar}} = 2.0\) using 1–4 homogenization passes. Objective function values showed that at least four passes were required to achieve these targets (Table 2). Experimental implementation of the optimal solution for four passes produced very good agreement with the target distribution (Figure 4).

Finally we considered the case where \(\mu = 0.8\) mm and \(\sigma^2 = 0.8\) mm\(^2\). Because the target mean drop size was relatively large, only two passes were required to achieve the resulting target distribution (Table 4). Although some model error was evident, experimental implementation of the optimal solution for two passes produced acceptable agreement with the target distribution (Figure 5).

4. CONCLUSION

A population balance equation (PBE) model that accounts for drop breakage and coalescence in high pressure homogenization was used for emulsion product design. Mechanistic functions allowed PBE model to have predictive capability over range of processing conditions. Six adjustable

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**Table 2. Model predicted and experimental results for the target \(d_{32} = 0.3\) and \(PD = 2\)**

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>(d_{32})</th>
<th>(PD)</th>
<th>(\Psi_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st} pass</td>
<td>2\textsuperscript{nd} pass</td>
<td>3\textsuperscript{rd} pass</td>
<td>4\textsuperscript{th} pass</td>
</tr>
<tr>
<td>1000</td>
<td>—</td>
<td>—</td>
<td>0.617</td>
</tr>
<tr>
<td>1000</td>
<td>645</td>
<td>—</td>
<td>0.410</td>
</tr>
<tr>
<td>1000</td>
<td>740</td>
<td>280</td>
<td>0.340</td>
</tr>
<tr>
<td>1000</td>
<td>846</td>
<td>353</td>
<td>0.308</td>
</tr>
<tr>
<td>1000</td>
<td>846</td>
<td>353</td>
<td>0.306</td>
</tr>
</tbody>
</table>

**Table 3. Model predicted and experimental results for the target \(\mu = 0.5\) and \(\sigma^2 = 0.8\)**

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>(\Psi_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st} pass</td>
<td>2\textsuperscript{nd} pass</td>
</tr>
<tr>
<td>1000</td>
<td>—</td>
</tr>
<tr>
<td>1000</td>
<td>414</td>
</tr>
<tr>
<td>1000</td>
<td>356</td>
</tr>
<tr>
<td>1000</td>
<td>112</td>
</tr>
<tr>
<td>656</td>
<td>107</td>
</tr>
</tbody>
</table>

**Fig. 3. Interpolated model parameters using \(K_2\) (×) and \(K_4\) (△) values obtained at four different pressures.**

\[
\Psi_1 = \sqrt{\frac{(d_{32\text{tar}} - d_{32})^2}{d_{32\text{tar}}^2} + \frac{(PD_{\text{tar}} - PD)^2}{PD_{\text{tar}}^2}}
\]

where the \(\text{tar}\) subscript represents target values and the other variables represent model predicted values. While these target values are relatively simple to specify for a particular problem, their attainment does not ensure that a satisfactory drop size distribution will be achieved. Therefore, the second objective involves the full distribution:

\[
\Psi_2 = \sum_{j=1}^{n} \left[ \frac{n_{\text{tar}}(v_j) - n_p(v_j)}{n_{\text{tar}}(v_j)} \right]^2
\]

where \(n_{\text{tar}}\) is the target volume density and \(n_p\) is the model predicted volume density. The PBE model was spatially and temporally discretized to generate a nonlinear algebraic equation system that was posed as equality constraints in the optimization problem. The homogenization pressure was constrained to be between 100 and 1000 bar. Given a specified objective and a fixed number of homogenization passes, the problem of determining the optimal pressure at each pass was solved within AMPL using the nonlinear optimization code CONOPT.

**3.2 Results**

First we considered the problem of achieving a drop size distribution with \(d_{32\text{tar}} = 0.3\) mm and \(PD_{\text{tar}} = 2.0\) using 1–4 homogenization passes. Objective function values showed that at least four passes were required to achieve these targets (Table 2). Experimental implementation of the optimal solution for four passes showed very good agreement with the predicted results.

Specification of a target drop size distribution for minimization of the \(\Psi_2\) objective is more challenging. Our experience is that normal-like distributions are achievable when the drop size is represented in logarithmic coordinates (see Figure 1). Therefore, target distributions were generated from the normal distribution by specifying the mean (\(\mu\)) and variance (\(\sigma^2\)). First we considered the case where
Table 4. Model predicted and experimental results for the target $\mu = 0.8$ and $\sigma^2 = 0.8$

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>$\psi_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st pass</td>
<td>Model predicted</td>
</tr>
<tr>
<td>100</td>
<td>0.034</td>
</tr>
<tr>
<td>263</td>
<td>0.010</td>
</tr>
<tr>
<td>100</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Fig. 5. Model predicted and experimental distributions obtained with two optimized homogenization passes for the target $\mu = 0.8$ and $\sigma^2 = 0.8$.

parameters were estimated by nonlinear optimization from measured drop volume distribution at specified base case condition. The values of parameters $K_2$ and $K_1$ were interpolated to generate improved results over broad range of homogenization pressure. Two optimization objectives that differ with respect to the distribution specifications were formulated. Using PBE model, number of homogenization passes and optimal pressure corresponding to each pass were obtained for different target drop size distributions. After experimentally implementing the optimal solutions, we found that experimental results showed very good agreement with target distribution properties.

REFERENCES


