

INVESTIGATION OF DISCRETE POPULATION BALANCE MODELS AND ITS PARAMETERS FOR TURBULENT EMULSIFICATION PRO- CESSES.

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Abstract. Different challenges and limitations occur with the simulation of liquid/liquid dispersion using population balance equations (PBE). A limitation is that the breakage and coalescence kernels tend to be specific to the equipment and scale used to acquire the evaluation data. It is reported in literature that PBE simulations are highly scale dependent. Once information is obtained using PBE, it cannot be used, with confidence, for scale-up [1]. Not every influence parameter of the drop size found its application already in the existing models. The concentration of surfactants or other surface active agents is the most obvious example. Generally, an additive or unintended ‘impurity’ can have a profound impact on the drop size. This influence is most often applied by the variation of the model parameters, which led to a broad variety of parameters reported in literature. Experimental results are compared with optimized PBE simulations. The achieved PBE parameter results are critically evaluated and compared with numerous parameter values from literature. A strong interdependency between the coalescence and breakage parameter was found

Keywords: population balance equation, liquid/liquid dispersion, modeling, parameter optimization

1. ANALYSIS AND MODELING OF AGITATED LIQUID/LIQUID DISPERSIONS

The properties of liquid/liquid (l/l) dispersions have been an active field of scientific studies since the 1950s [2]. Many excellent reviews are available [1-4]. These summarize the experimental work that was carried out to determine and to understand the influence parameters on the drop size distribution and mostly on the Sauter mean diameter ($d_{32} = \Sigma d_i^3 / \Sigma d_i^2$). This diameter is the ratio from the third and the second moment of the distribution and is directly related to the dispersed phase fraction ϕ_d and the total interfacial area per total volume a_f in the system ($d_{32} = 6\phi_d / a_f$).

In most of the reviewed cases, the experimental data has been correlated using a functional form based on the turbulence theory [5]. It was postulated that a drop would break up at a critical Weber number ($We = \rho_c n^2 D^3 / \gamma$). The Weber number is the ratio between external deformation forces provided by the stirrer (n - stirrer speed, D - impeller diameter) and the drop restoring forces associated with the interfacial tension γ . With the knowledge of this critical Weber number the drop size is predictable ($d_{32} \sim We^{-0.6}$).

For the analysis of the time evolution of a drop size distribution, population balance equations (PBE) are mostly applied. Population balances may be regarded either as an old subject that has its origin in the Boltzmann equation more than a century ago, or as a newer one in the light of growing variety of applications in which engineers have put it to practice. The methodology of population balances is indispensable for a rational treatment of dispersed phase processes in engineering. It is the capacity of population balances to address the evolutionary aspects of a dispersion [6].

The PBE in l/l systems define how populations of separate drops develop in the specific properties over time. They are analogous to material balances, but instead of applying them to each chemical species, they are applied to drop size class comprising the entire drop size distribution (DSD). Therefore, sink and source terms are referred to as birth and death rates by breakage and coalescence for a drop of a specific size [1].

Analytical solutions of the PBE exist only for unreasonably simplistic assumptions [1]. Because numerical methods have grown in reliability and flexibility they are the technique commonly used by many investigators to solve the PBE. Many other numerical solution methods are described in literature [7, 8]. However, a commercial solver for the PBE is PARSIVAL[®] (PARTicle SIZE eVALuation). It uses the Galerkin h-p method, which is based on a generalized finite-element scheme with self-adaptive grid and order construction. The mathematical details are given by Wulkow et al. [9]. PARSIVAL[®] is used as the PBE solver for all simulations associated with this study.

2. CHALLENGES AND LIMITATIONS USING PBE

Despite the fact that the PBE technology has been used by the chemical engineering community since the 1960s and that commercial software to solve the equation are available, little practical industrial use has been made of it for l/l dispersions. Part of this is due to the difficulty in obtaining quality drop size data which is suitable for quantitative model evaluation. A photo-optical measurement technique was used for this work [10] using automated image analysis for the drop detection [11].

A general solution of population balance equation does not exist, or only for unreasonably simplistic assumptions. For practical relevant cases different numerical solutions are possible. The verification of the possibility of reaching different computational optima is discussed in Figure 1. For a detailed description of the PBE equations describing the different models, please see [12] or the original sources.

Simulated Sauter mean diameters for $\varphi_d = 0.1$ at three different stirrer speeds (400, 550 and 700 rpm) are plotted in comparison to experimental data. The experimental data are from the studies by Gäbler et al. [13]. The experiments were conducted in a baffled-glass vessel with a diameter T of 150 mm equipped with a Rushton turbine of $D/T = 0.33$. Toluene was used as dispersed phase and water as continuous phase. The coalescence was decreased but not completely hindered by increasing the pH to 13.

The simulation data are reproductions from [13] and own studies using the equations from [14]. The used parameters for the associated simulations are listed in Table 1. The description of the simulations ((a) to (d)) follows the description in Figure 1. Four different simulation results are compared to one set of experimental data in Figure 1 (a) - (d). The simulations, which are all aiming to reflect the experimental measurements, were carried out using the complete model of [14] for a well mixed assumption as in the work of Gäbler et al.

Table 1. Parameter listing for the simulation results presented in Figure 1, br - breakage; coa - coalescence.

simulation	$c_{1,br}$ [-]	$c_{2,br}$ [-]	$c_{1,coa}$ [-]	$c_{2,coa}$ [m ²]	$c_{1,br} / c_{1,coa}$ [-]	source
(a)	$6.14 \cdot 10^{-4}$	$5.70 \cdot 10^{-2}$	$1.50 \cdot 10^{-4}$	$2.56 \cdot 10^{12}$	$4.1 \cdot 10^0$	Gäbler et al. (2006)
(b)	$2.33 \cdot 10^{-3}$	$3.08 \cdot 10^{-2}$	$5.68 \cdot 10^{-4}$	$7.11 \cdot 10^{12}$	$4.1 \cdot 10^0$	this study
(c)	various, see Figure 1	$3.08 \cdot 10^{-2}$	$c_{1,br} \cdot 4.1^{-1}$	$7.11 \cdot 10^{12}$	$4.1 \cdot 10^0$	this study
(d)	$5.31 \cdot 10^{-3}$	$4.50 \cdot 10^{-2}$	$2.18 \cdot 10^2$	$8.53 \cdot 10^{14}$	$2.4 \cdot 10^{-5}$	this study

Simulation (a) is reproducing the results from [13]. The same prediction accuracy is achieved with a completely different set of parameters with simulation (b). It has to be mentioned, that both parameter sets are in the same order of magnitude (see absolute values in Table 1 for (a) and (b)). Opposed are the results for the parameters of simulation (d). The coa-

lence parameters are two orders larger and $c_{1,br}$ is one order larger than in the two other parameter sets. The simulation results are in a comparable range of prediction quality although the results for the lower stirrer speed are less satisfying. This may be a widely familiar result of the fortuitous fall of the solution in different local optima.

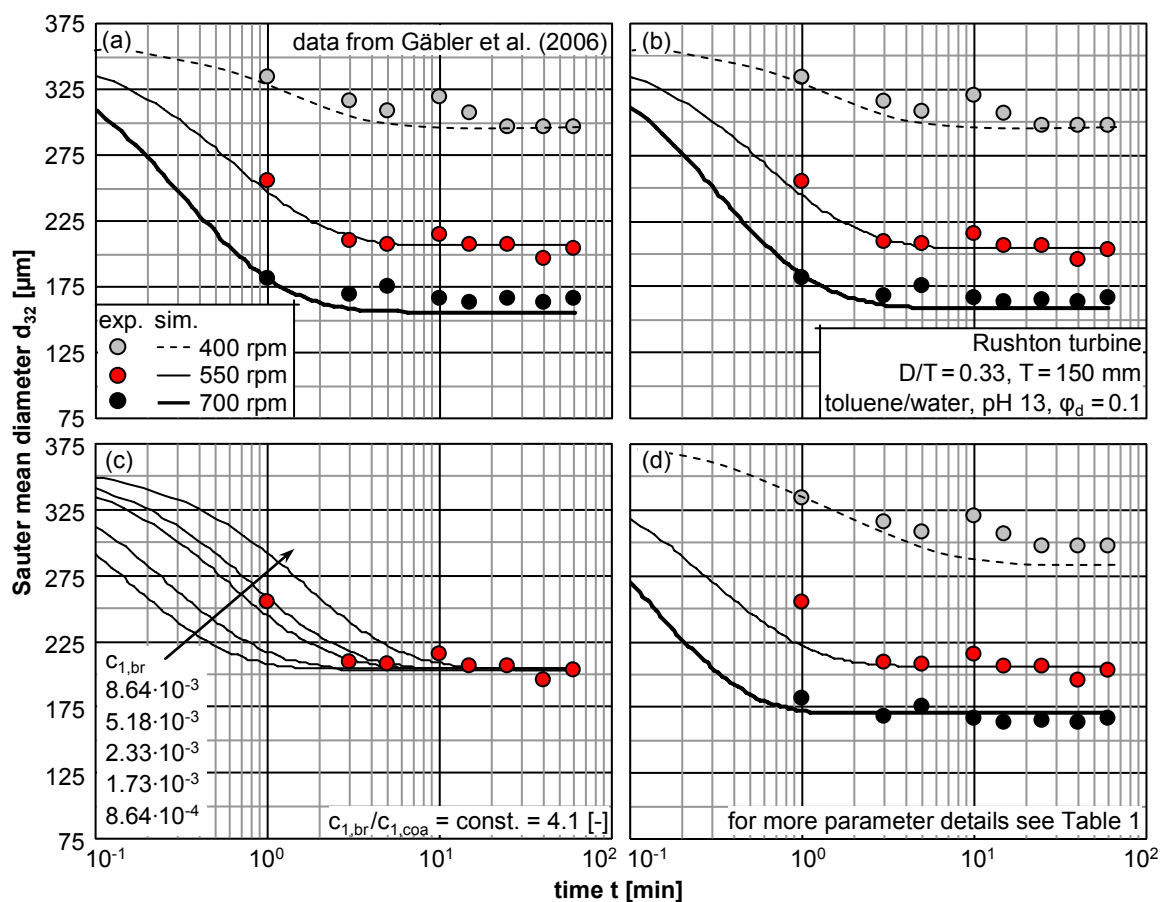


Figure 1. Comparison of one set of experimental data (symbols) from Gäbler et al. [13] and various simulations with different model parameter (lines): (a) - simulations using the parameters from [13], (b) - simulations using own optimized parameters achieving the same accuracy as [13], (c) - simulations varying $c_{1,br}$ for a constant ratio between $c_{1,br}/c_{1,coa}$ using the parameters from simulation (b) as initial values for the variation, (d) - simulations using a third parameter combination with strong differences compared to the used values in (a) and (b).

The results shown in Figure 1 (c) may additionally uncover some correlations between the parameters. The ratio between $c_{1,br}$ and $c_{1,coa}$ was kept constant at the same value resulting from the parameter values by [13]. As it can be seen from Figure 1 (c) the strong variation of $c_{1,br}$ (by a factor of 10) is not influencing the steady state result of d_{32} if the ratio between $c_{1,br}$ and $c_{1,coa}$ was kept constant. This is in excellent agreement with the results by [15] who found the same dependency and reported a value of around 4.7 for the ratio between these parameters, which supports a physically interpretable interdependence between the kinetics of the breakage and coalescence processes [15].

They explain that behavior by the fact that steady state batch conditions imply a virtually infinite residence time, which means that it is impossible to set a definite time scale. This is only true, if only the steady state results are interpreted as done by [15]. The results here show a significant influence on the time to achieve the same steady state value for d_{32} . As larger the value of $c_{1,br}$ is as faster reaches the simulation the steady state. That shows for the selected example, that the breakage kinetic (employed by $c_{1,br}$) is of higher impact than the coalescence one. This interconnection between the different parameters together with the influence of the broad variance of the parameter sets are shown in the following paragraphs. Many parameters

differing in several orders of magnitude are used in literature to adapt the models to experimental results. As mentioned above, breakage and coalescence terms influence each other and therefore different mathematical solutions are possible to display the same set of experiments.

A detailed parameter review was carried out in this study for the model of Coulaloglou and Tavlarides [14]. Only values used for the simulation of l/l system have been taken into account. The results are displayed in Table 2. The values scatter dramatically, only the variance of the values for $c_{1,br}$ is smaller as their average value. This results are disturbing because only the influence of the coalescence parameter $c_{2,coa}$ is known as almost uninfluential on the drop size compared to the other parameters.

Table 2. Parameter listing from literature for the empirical constants in the drop breakage and drop coalescence rate function of Coulaloglou and Tavlarides (1977).

	$c_{1,br} [10^{-1}]$	$c_{2,br} [10^{-1}]$	$c_{1,coa} [10^{-1}]$	$c_{2,coa} [m^2]$
[14]	3.360	1.06	0.0022	$2.28 \cdot 10^{13}$
[16]	0.049	0.8	0.0022	$3.00 \cdot 10^{12}$
[17]	0.103	0.635	0.0045	$1.89 \cdot 10^{13}$
[18]	0.049	0.551	0.0022	$2.00 \cdot 10^9$
[19]	0.049	0.8	0.019	$2.00 \cdot 10^{12}$
[20]	0.049	0.558	0.017	$4.74 \cdot 10^{12}$
[15]	0.021	0.318	0.0045	$6.41 \cdot 10^{12}$
[15]	0.047	0.318	0.01	$5.45 \cdot 10^{12}$
[21]	0.06	0.011	-	-
[13]	0.006	0.57	0.0015	$2.56 \cdot 10^{12}$
[12] (1-Zone)	0.034	0.756	2.91	$3.58 \cdot 10^{17}$
[12] (2-Zone)	0.14	3.33	2.91	$3.58 \cdot 10^{17}$
[22]	0.39	3.33	2.91	$4.64 \cdot 10^{18}$
[23]	0.119	2.75	-	-
[24]	10.0	41.0	1.0	$1.00 \cdot 10^9$
[25]	8.6	41.0	0.4	$1.00 \cdot 10^{10}$
this study - simulation (b)	0.023	0.308	0.0057	$7.11 \cdot 10^{12}$
this study - simulation (d)	0.053	0.45	2180.0	$8.53 \cdot 10^{14}$
average value	1.29	5.47	137.0	$3.35 \cdot 10^{17}$
variance $V(c_i)$	0.91	16.8	29600.0	$1.33 \cdot 10^{36}$
minimum value	0.006	0.011	0.0022	$1.00 \cdot 10^9$
maximum value	10.0	41.0	2180.0	$4.64 \cdot 10^{18}$

The interconnection between the different parameters is discussed in Figure 2. All literature values are plotted as a function of the breakage parameter $c_{1,br}$. Although the single values scatter a lot, some tendencies can be postulated.

The values of the breakage parameter used in literature show a vague tendency to a linear correlation ($c_{2,br} = 3 \cdot c_{1,br}$). That means with increasing breakage kinetic (equal to decreasing breakage times in this model), employed via $c_{1,br}$, a breakage probability is decreasing (employed as $\exp(-c_{2,br})$). This means, that the values used in literature for the breakage parameter partly balance each other. A fast kinetic is damped by a low probability and vice versa.

The same is true if the tendencies between $c_{1,br}$ and the coalescence parameters is analyzed. The increase of the breakage kinetic leads to an increase of the coalescence kinetic. Although the ratio between both parameters is scattering a lot, the tendency between them can be estimated by a linear correlation too ($c_{1,coa} = 0.7 \cdot c_{1,br}$).

An increase in $c_{2,coa}$ leads to a decrease in the coalescence efficiency the increase of $c_{1,br}$ leads to a decrease of $c_{2,coa}$. Again the opposed phenomena of drop breakage and drop coalescence partly balance each other. Of course these tendencies are qualitative. The proposed correlations are not suitable to predict single parameter values as a function of the other one. However, the results support the assumption, that several local optima are possible for the same application. That is the major reason, why it is hard to analyze the pure physics behind the model approaches. The mathematical background needs always be reflected.

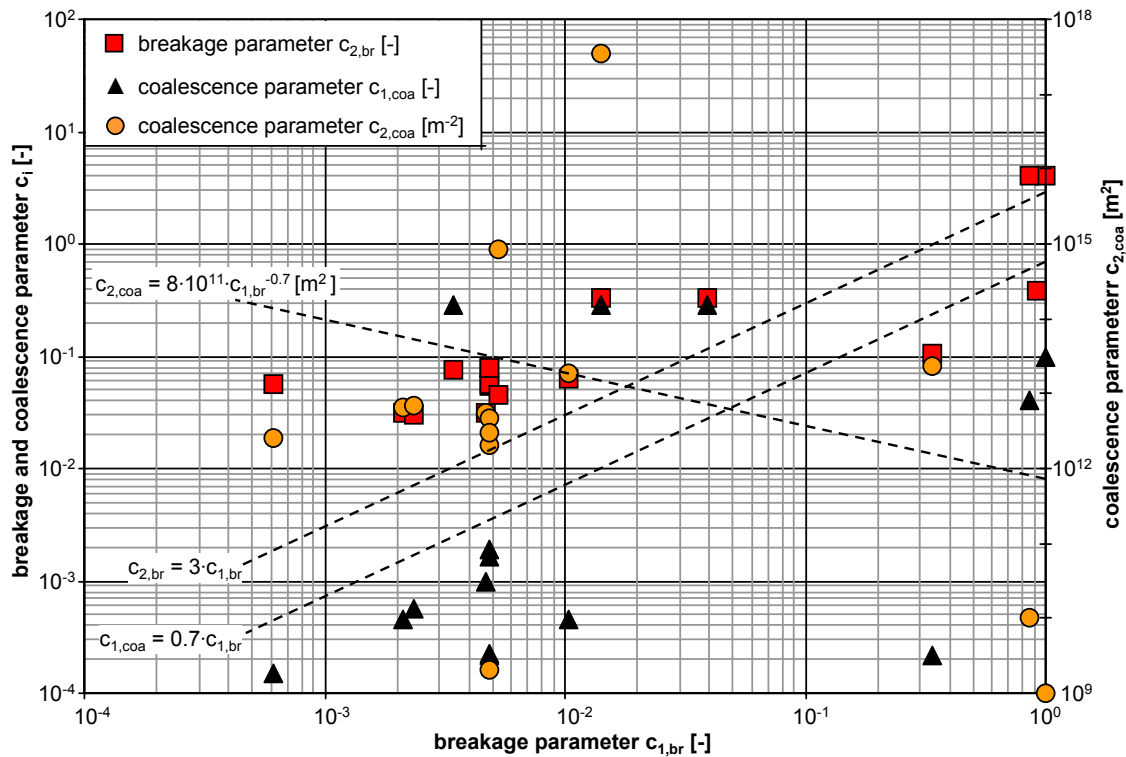


Figure 2. Dependency of literature values of the parameters $c_{2,br}$, $c_{1,coa}$ and $c_{2,coa}$ from the model of Coualoglou and Tavlarides (1977) on the breakage parameter $c_{1,br}$.

The used experimental set-up is a working section of several static mixers which alternate with the same number of rest zones. Each of these zones is modeled as a number of compartments with homogenous energy dissipation within these compartments. Note that the number of compartments used for the description of the breakage and coalescence dominated zone is not presented by Azizi and Al Taweel [24, 25]. However, the development of the used energy dissipation rates in the different zones is presented by [25]. The value ranges from $1 \cdot 10^{-1}$ to $1.4 \cdot 10^4 \text{ m}^2/\text{s}^3$. The use of these local values implements a more detailed physical description of the process in the model. It is in contradiction to the commonly used well mixed simplification with only one average value for ε .

This postulation is in accordance with own achieved values. Two sets of parameters are reported in [12]. One was estimated for the well mixed condition, the other was estimated after a separation of the system into a stirrer and a bulk region, following the multi zone approach by Alopaeus et al. (1999). The differences between experimental data and PBE simulations have been minimized for both approaches, the values for the 2-zone model are four times higher than the values for the 1-zone model.

3. CONCLUDING REMARKS

Population balances have become a powerful tool in chemical engineering over the last decades. Developing computer technologies have facilitated robust numerical solution methods which can be coupled with CFD to base the calculations on precise description of the fluid dynamics.

Nevertheless, the increasing number of contradicting models, reported values of model parameters and the lack of evaluated experimental data from the broad variety of industrial applications limit the use of PBE in industrial practice.

To avoid a local optimum, simultaneous fitting of the different parameters, the use of different initial values and a broad variation of the physical system are necessary but still no guarantee for an accurate description. Transient measurements should be given a high weight in

the fitting process in order to identify especially the breakage parameters properly. Still the fitting of PBE parameters is a major challenge

Furthermore, the reported missing of objective solutions of the PBE interferes with the precise determination of coalescence and breakage models. However, this is the key challenge to be able to formulate trustful predictive PBE models [26].

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