Development, Validation and Application of a Computer Code to Solve Population Balance Equations for Liquid-Liquid Dispersion by QMOM

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Use of Quadrature Method of Moments (QMOM) to solve population balance equations is a computationally economical way to estimate Sauter mean diameter of liquid-liquid dispersions. In the present work, a code is written to solve population balance equations by QMOM using adaptive Wheeler algorithm. The code is validated by comparing its predictions with reported analytical results for the cases of pure aggregation and pure breakage. The code is then used for predicting Sauter mean diameter of liquid-liquid dispersion in a continuous flow stirred tank.

Keywords: Population balance, QMOM, Stirred tank, Sauter mean diameter

Introduction

Performance of multiphase operations like crystallization, liquid-liquid extraction and multiphase reactions depends on the specific interfacial area between the phases. Thus particle size or drop size which evolves due to phenomena like breakage, aggregation, growth etc. plays a major role in these processes. Therefore, it is important to predict drop size or particle size. Population balance equations which account for the phenomena like breakage, aggregation, growth etc., are continuity statements that can be solved to predict the drop or particle size. These equations are written in terms of an internal coordinate (viz. particle volume or characteristic length). There are two main methods to solve population balance equations. These are the method of classes and the method of moments. In the method of classes, the internal coordinate is discretized into a finite series of bins, and corresponding frequency is estimated to generate drop or particle size distribution. In the method of moments, the internal coordinate is integrated and drop or particle size is evaluated through moments. Method of classes is a direct, simplistic but computationally demanding approach which predicts population density directly whereas method of moments is a computationally economical approach which gives representative drop diameter and is useful for coupling with a Computational Fluid Dynamics (CFD) code[1,2]. The number of equations solved in the method of classes can be much higher than the number of equations solved in the method of moments. There are several methods of moments and quadrature method of moments (QMOM) is one of them. QMOM, proposed by McGraw, 1997[3] for aerosol modeling, has also been extended for breakage and aggregation problem[1] which is the case in liquid-liquid extraction. QMOM is basically a presumed particle size distribution method in which the distribution is assumed to be Gaussian.

The aim of this work is to solve population balance equations using QMOM to obtain Sauter mean diameter of liquid–liquid dispersion generated in a homogeneous continuous-flow stirred tank. A code accounting for breakage and coalescence has been written for this purpose. For validating the code, the predictions of the code for the cases of pure breakage and pure aggregation are compared with available analytical results.

Mathematical model

Population balance equations for the method of moments

Drop size distribution of liquid-liquid dispersion in a continuous-flow stirred tank depends on the drop size distribution in the feed, breakage and coalescence of droplets inside the tank. In a process involving mass transfer swelling or shrinking of droplets due to mass transfer is also present though it can be ignored for hydrodynamic study without mass transfer. The population balance equation for characteristic length of drop (L) in a homogeneous control volume can be written as[1]

$$\frac{d}{dt}\{n(L;t)V\} = n_{in}(L;t)Q_{in} + B^a(L;t) - D^a(L;t) + B^b(L;t) - D^b(L;t) - n(L;t)Q_{out} \quad (1)$$

Here B^a and B^b are birth rates of droplet of size L at any time t due to aggregation and breakage, respectively. D^a and D^b are the death rates of droplet size L at any time t due to aggregation and breakage, respectively. V is the volume of the control volume and Q_{in} is the inlet flow rate and Q_{out} is the outlet flow rate. $n(L;t)$ is the number of droplets having characteristic length L per unit volume at any time t and $n_{in}(L;t)$ is the number of droplets with characteristic length L per unit volume of the inlet stream at any time t. Population balance equation can be re-written as Eq. 2 for a batch system.

$$\frac{d}{dt}\{n(L;t)V\} = B^a(L;t) - D^a(L;t) + B^b(L;t) - D^b(L;t) \quad (2)$$

The expressions for the birth and death rates are given by Eq. (3) to (6)[4].

$$B^a(L;t) = \frac{L^2}{2}\int_0^L \frac{\beta\{(L^3-\lambda^3)^{1/3},\lambda\}}{(L^3-\lambda^3)^{2/3}} n\{(L^3-\lambda^3)^{1/3};t\} n(\lambda;t)d\lambda \quad (3)$$

$$D^a(L;t) = n(L;t)\int_0^\infty \beta(L,\lambda)n(\lambda;t)d\lambda \quad (4)$$

$$B^b(L;t) = \int_L^\infty a(\lambda)b(L|\lambda)n(\lambda;t)d\lambda \quad (5)$$

$$D^b(L;t) = a(L)n(L;t) \quad (6)$$

Where, β is the aggregation (coalescence) kernel, a is the breakage kernel and b is the daughter droplet distribution. In literature, several kernels have been reported. The right combination of the kernels may change from system to system. To solve Eq. 1 or Eq. 2 using QMOM a further transformation is needed i.e. aggregation, breakage and other terms present in Eq. 1 must be written in terms of moment. Moment transformation is done by applying Eq. 7 which defines the k^{th} order moment.

$$m_k(t) = \int_0^{+\infty} n(L;t)L^k dL \quad (7)$$

Eqs. (3)-(6) are substituted into Eq. (1) and then integrated with respect to L after multiplying with L^K. Assuming $Q_{in} = Q_{out}$ the equation of k^{th} moment can be written as

$$\frac{dm_k}{dt} = m_{kin}/\tau + \frac{1}{2}\int_0^{+\infty} n(\lambda;t)\int_0^{+\infty}\beta(u,\lambda)(u^3+\lambda^3)^{k/3}n(u;t)du d\lambda - \int_0^{+\infty}L^k n(L;t)\int_0^{+\infty}\beta(L,\lambda)n(\lambda;t)d\lambda dL + \int_0^{+\infty}L^k\int_0^{+\infty}a(\lambda)b(L|\lambda)n(\lambda;t)d\lambda dL - \int_0^{+\infty}L^k a(L)n(L;t)dL - m_k/\tau \quad (8)$$

Second term in the right hand side of Eq. 8 is derived by assuming a variable "u" such that $u^3 = L^3 - \lambda^3$ and thus $dL = \frac{u^2}{L^2}du$.

Application of QMOM and discretization

Eq. 8 is a non-linear integro-differential equation, which can be solved using quadrature approximation with adaptive Wheeler algorithm[4], which determines weights (w_i) and abscissas (L_i) from the moments. The algorithm is based on the minimization of the error by replacing integral of Eq. (7) with its quadrature approximation as given in Eq. (9). Adaptive wheeler algorithm determines $N/2$ weights and $N/2$ abscissas from N moments by finding eigenvalues and eigenvectors. Discretized form of Eq. 8 is shown in Eq. 10.

$$m_k = \int_0^{+\infty} n(L)L^k dL \approx \sum_0^N w_i L_i^k \quad (9)$$

$$\frac{dm_k}{dt} = m_{kin}/\tau + \frac{1}{2}\sum_{i=1}^{N/2} w_i \sum_{j=1}^{N/2} w_j (L_i^3 + L_j^3)^{\frac{k}{3}}\beta_{ij} - \sum_{i=1}^{N/2} L_i^k w_i \sum_{j=1}^{N/2}\beta_{ij}w_j + \sum_{i=1}^{N/2} a_i b_i^{(k)} w_i - \sum_{i=1}^{N/2} L_i^k a_i w_i - m_k/\tau \quad (10)$$

Where $\beta_{ij} = \beta(L_i, L_j)$; $a_i = a(L_i)$ and $b_i^{(k)} = \int_0^{+\infty} L^k\, b(L|L_i)dL$.

Results and discussion

Validation with analytical results

QMOM-based population balance model is solved for the cases for which analytical solutions exist to check the accuracy of the code. Two cases- only aggregation and only breakage – are solved.

Case 1: This case corresponds to pure aggregation in a batch stirred tank. A constant aggregation kernel is used which is represented by $\beta_{ij} = 1$. Due to the absence of breakage, $a_i = 0$ and daughter droplet distribution is not required. The analytical solution for this case is given by Eq. 11[2].

$$m_k = m_{k0}\left[\frac{2}{2+N_0\beta(L,\lambda)t}\right]^{\left[1-\left(\frac{k-1}{3}\right)\right]} \quad (11)$$

Case 2: No aggregation is assumed. Breakage kernel is proportional to volume of the particle and daughter droplet distribution is assumed to be uniform. Analytical solution for the moments for this case is given by Eq. 12[2].

$$n(L) = 3L^2(1+t)^2 e^{-L^3(1+t)} \quad (12)$$

For both the cases, assumed initial drop size distribution is given by Eq. 13. N_0 and v_0 are number of drops per unit volume and volume of the domain of interest and t is time. Values of N_0 and v_0 are $1/m^3$ and $1\ m^3$, respectively.

$$n_0(L) = 3L^2\frac{N_0}{v_0}e^{-L^3/v_0} \quad (13)$$

Comparison of analytical results with the results obtained from our code for the two cases are shown in Fig. 1 and Fig. 2. It should be noted that the third moment, which represents volume of the dispersed phase, is constant over time as the volume of the dispersed phase remains conserved.

Prediction of Sauter mean diameter for a continuous flow stirred tank

After validation, the code is used to predict drop Sauter mean diameter of liquid-liquid dispersion in a continuous flow stirred tank. The liquid-liquid system is wet phosphoric acid dispersed in a mixture of di-2-ethyl hexyl phosphoric acid (D2EHPA), tributyl phosphate (TBP) and dodecane. This phase system is important for recovery of uranium and other

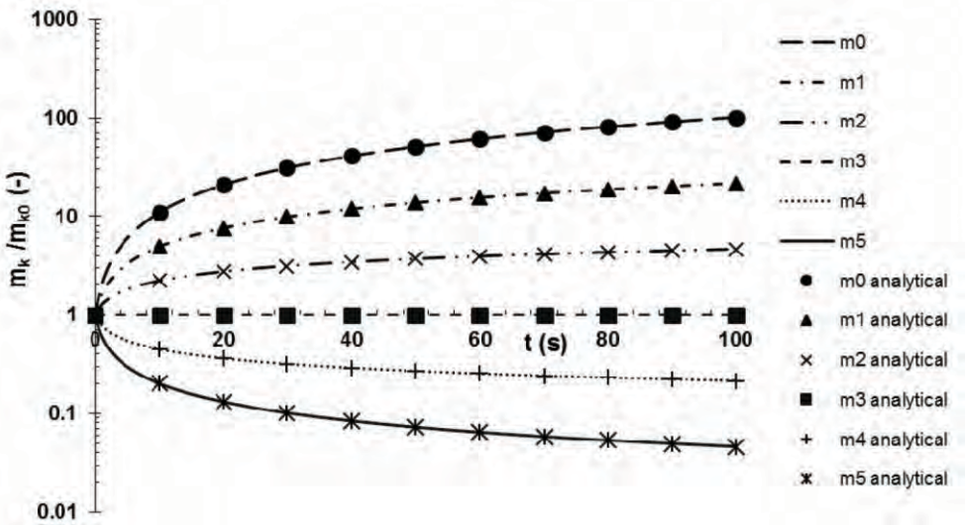

Fig. 1: Validation of the QMOM-based population balance code for only aggregation process in a batch stirred tank

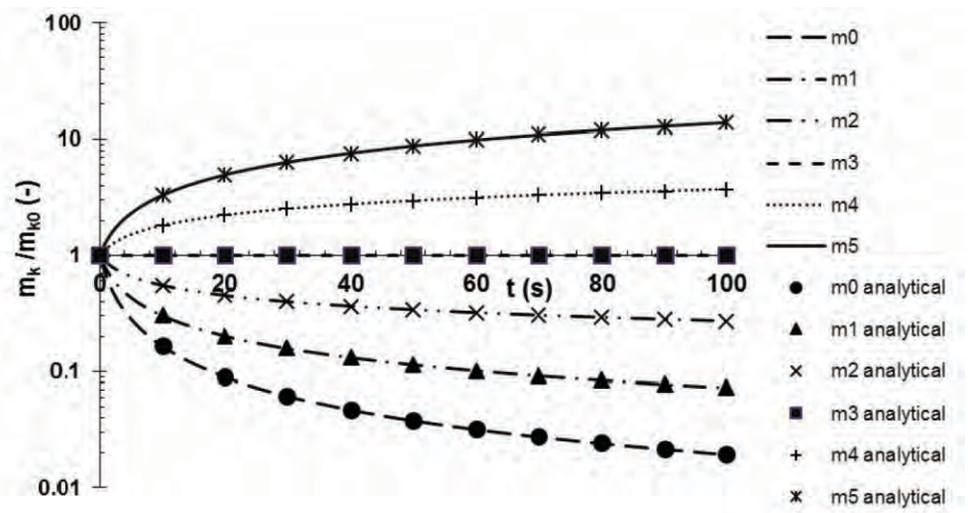

Fig. 2: Validation of the QMOM-based population balance code for only breakage process in a batch stirred tank

rare earths from phosphoric acid[6,7]. The experimental data about the quality of dispersion and population balance modeling using method of classes have been reported earlier[8,9]. Breakage and aggregation kernels proposed by Coulaloglou & Tavlarides, 1977[10] and symmetric daughter droplet distribution are used. Breakage kernel, aggregation kernel are given by Eqs. 14-15[10] and daughter droplet distribution are given by Eq. 16[5]. $h(L,\lambda)$ and $\eta(L,\lambda)$ are collision frequency and collision efficiency, respectively. Collision frequency is defined as rate of collision between two drops having characteristic length L and λ. Collision efficiency is defined as the probability of aggregation to form a new bigger drop on collision.

$$a(L) = C_1 \frac{\varepsilon^{1/3}}{(1+\phi)L^{2/3}} \exp\left\{-C_2 \frac{\sigma(1+\phi)^2}{\rho_d \varepsilon^{2/3} L^{5/3}}\right\} \quad (14)$$

$$\beta(L,\lambda) = h(L,\lambda)\eta(L,\lambda) = \left[C_3 \frac{\varepsilon^{1/3}}{(1+\phi)}(L+\lambda)^2\left(L^{2/3}+\lambda^{2/3}\right)^{1/2}\right] \exp\left\{-C_4 \frac{\mu_c \rho_c \varepsilon}{\sigma^2(1+\phi)^3}\left(\frac{L\lambda}{L+\lambda}\right)^4\right\} \quad (15)$$

$$b(L|\lambda) = \begin{cases} 2 & if\ L = \frac{\lambda}{2^{1/3}} \\ 0 & Otherwise \end{cases} \quad (16)$$

ε is th specific energy dissipation rate, ϕ is the dispersed phase hold up, ρ_d is the density of the dispersed phase, ρ_c is the density of the continuous phase, μ_c is the viscosity of the continuous phase and σ is the liquid-liquid interfacial tension.

To begin with, the constants of the kernels (C_1, C_2, C_3 and C_4) were optimized to minimize the error between predicted and experimentally measured Sauter mean diameter. A part of the experimental data was used for finding out the optimum value of the constants, remaining experimental data were used for

validation. Table 1 lists different values of the constants tried and corresponding error. Model 6 shows minimum error so it is used for the validation. The model with optimized constants (Model 6) is validated with another set of experimental data and error is found to be about 14%. Fig. 3 shows the

Table 1: Average error in prediction of Sauter mean diameter for different combinations of the values of the model constants

Model No.	C_1	C_2	C_3	C_4	Avg. Error
Model 1	0.45	1000	0.0005	0.0119	28.63%
Model 2	0.65	760	0.0005	0.0119	26.74%
Model 3	0.45	700	0.0005	0.0119	17.65%
Model 4	0.45	850	0.0005	0.0119	16.70%
Model 5	6.5	900	0.1	0.0001	15.49%
Model 6	4.7	900	0.1	0.0001	15.22%

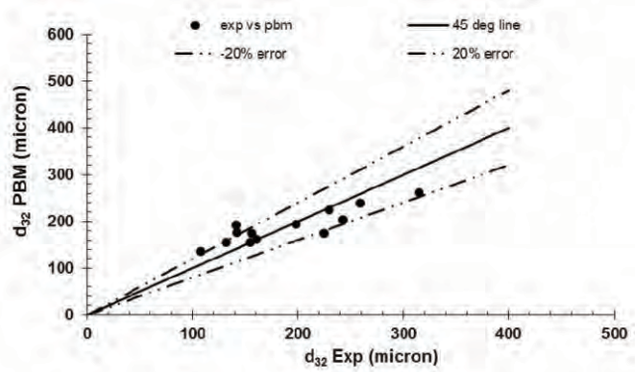

Fig. 3: Comparison of measured and predicted Sauter mean diameters of liquid-liquid dispersion in a continuous flow stirred tank

comparison of the Sauter mean diameters predicted by the code with the experimental Sauter mean diameters. The experimental data shown in Fig. 3 are the experimental data which were not used in optimization of model constants.

Conclusion

QMOM-based population balance code is written and validated by comparing its predictions with the analytical results for two special cases. The code is then used to estimate the Sauter mean diameter of liquid-liquid dispersion in a continuous flow stirred tank. The code with optimized values of constants of breakage and coalescence kernels is found to predict Sauter mean drop diameter with an average error of less than 15%. The code will be further extended to make it applicable for columnar contactors.

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