Mean Drop Size Correlations and Population Balance Models for Liquid—Liquid Dispersion

Mohd Izzudin Izzat Zainal Abidin, Abdul Aziz Abdul Raman, and Mohamad Iskandar Mohamad Nor
Dept. of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

DOI 10.1002/aic.14751
Published online February 16, 2015 in Wiley Online Library (wileyonlinelibrary.com)

Reliable models are required for accurate estimation of drop sizes which govern the interfacial area and rate of mass transfer in a system where various correlations and models have been improved for better accuracy and wider application breath. In this article, relevant semiempirical equations and population balance equation (PBE) models are reviewed. Semiempirical correlations are highly system dependent and limited to prediction of steady-state drop size while PBE models could estimate transient drop size with considerations of inhomogeneity and flow spatial variation during drop size evolution. With appropriate model parameters determination, different PBE models can be used to reproduce experimental data for a similar system. © 2015 American Institute of Chemical Engineers AIChE J, 61: 1129–1145, 2015

Keywords: drop sizes, liquid–liquid dispersion, semiempirical equation, population balance equations, flow spatial variation

Introduction

Liquid–liquid dispersion is a process of dispersing one liquid into another in the form of small drops where both liquids are completely immiscible to create a system with distribution of drop sizes. It is a common operation in industrial processes involving mass transfer such as emulsification, extraction, and reactive dispersion.1,2 The drop size distribution (DSD) determine the available interfacial area that controls the amount of heat and mass transferred between liquids.3 As a result, the interfacial area and other transport parameters related to it can be controlled by manipulating the distribution of drop sizes. Therefore, it is important to have detailed knowledge on the evolution of drop sizes for accurate prediction of mass-transfer rate and reaction rate in liquid–liquid systems.4

Dispersion is a complex process involving a large number of parameters including hydrodynamics phenomena, turbulence structure, and natural physiochemical effects.5 Drop breakage and coalescence process in turbulent dispersions have been subjects to theoretical and experimental attention over the past years. The physical and chemical phenomena taking place in stirred vessels are largely influenced by transient drop sizes while the equilibrium DSD determines the properties of the end product.6 Therefore, information on drop sizes for both transient and steady states are important.

Numerous studies have been conducted to investigate the influence of different parameters on the evolution of drop sizes and mean drop size, which lead to development of various drop size models. These include semiempirical correlation which relates mean drop size to different parameters and population balance equation (PBE) to simulate the actual dispersion process. The steady-state drop sizes are commonly correlated by semiempirical equation while transient drop size is estimated by PBE. Subsequently, such correlations have been refined with considerations from improvements in techniques that could eliminate restrictive assumptions and the ability to solve complex processes without error-prone assumptions.

Various semiempirical equations and submodels in PBE for drop size predictions in turbulent flow are reviewed in this article with focus on models that have been successfully applied and frequently cited in the literature. Earlier correlations and models however are restricted by various assumptions which limit its applications. Therefore, many studies were conducted which result in modification of correlations and models for improvements.

Detailed descriptions on breakage and coalescence functions for fluid particles in turbulent flow have been reported in reviews by Liao and Lucas7,8 and Solsvik et al., (2013).9 While more novel models were developed recently, this article aims to review the improved models which could overcome the limitations of earlier models. This article also includes the discussion on model parameters determination and accounting for nonhomogeneity in the system. Challenges regarding the modeling of dispersion process with possible solutions are discussed.

Mechanism of Drop Formation

Drop breakage and coalescence occur simultaneously during dispersion process where both phenomena have to be considered and the final drop sizes in the dispersion is the result of competition between both processes.10
Drop breakage mechanism

Drop breakage in moving fluids is caused by the interactions between mechanical forces and resistance from surface and internal viscous forces. A drop immersed in moving liquid experience external forces from the surrounding fluids which tend to cause deformation by promoting instabilities. The external forces caused drop to stretch, elongate, and eventually split if the kinetic energy is sufficient to overcome the drop’s resisting forces. Therefore, drop breakage only occurs when adequate energy is obtained to compensate for increment in surface energy caused by increase in the drop’s total surface area. As a result, drops below a maximum size, \( d_{\text{max}} \) are unbreakable as their cohesive forces are large enough to resist deformation. The value of \( d_{\text{max}} \) depends on the flow field conditions and drop’s physical properties.

Disruptive and Cohesive Forces. In turbulent flows, drop breakage is caused by turbulent pressure fluctuations, viscous shear stress, and interfacial instability. At low continuous phase viscosity and high impeller speed, turbulent pressure fluctuations is the dominant breakage mechanism. The turbulent force, \( \tau_c \) causes velocity change across the drop’s surface over a distance equal to its diameter, \( d \). It is proportional to the root mean square of velocity fluctuation across a distance \( d \) and is written as

\[
\tau_c \propto \rho_d u^2(d) \tag{1}
\]

The mean velocity difference is given as

\[
u^2(d) = k^{1/2}(\epsilon_d)^{1/3} \tag{2}
\]

The value of constant \( k \) in Eq. 2 for stirred vessels is reported to be in the range of 2.0-8.2 where the different values of \( k \) are summarized by Ghasempour et al., (2014). For simplification, it is assumed that only turbulent structure which is equal or smaller than the particle size could cause drop breakage while larger turbulent structure only causes translation displacement in the direction of the turbulence. The assumption however could be eliminated in the modeling of PBE.

The cohesive forces which resist deformation and restore drops to their original shape are surface energy and internal viscous force which are controlled by the drop’s physical properties. At low dispersed phase viscosity, the contribution of internal viscous force is small and can be assumed to be negligible. However, as viscosity increases, the internal viscous force has significant influence on drop’s resistance against breakage.

The mechanism of drop breakage in turbulent flows can be expressed as a balance between turbulent force, \( \tau_c = C_1 \rho_d u^2(d)/d^{1/3} \) and combined cohesive forces, \( \tau_c = \sigma/d \) and \( \tau_c = C_2 \mu_d (\epsilon_d/\rho_d)^{0.5}/d \). From interaction between forces, the extent of deformation or the relative resistance to breakup, \( E_R \) can be defined, which determines whether a drop will be broken into smaller drops

\[
E_R = \frac{E_s}{E_k} = \frac{\tau_c + \tau_c}{\tau_c} = \frac{C_1 \rho_d (N^2 D^2)^{1/3} d^{1/3} + C_2 \mu_d (\epsilon_d/\rho_d)^{0.5} (N^2 D^2)^{1/3} d^{1/3}}{C_1 \rho_d (N^2 D^2)^{1/3} d^{1/3}} \tag{3}
\]

Based on Eq. 3, the resistance against breakage depends on the physical properties of the drops which are interfacial tension, \( \sigma \) and viscosity, \( \mu_d \). If \( \mu_d \) is small with respect to unity, the drops resistance toward breakage is mainly contributed by interfacial tension.

Drop coalescence mechanism

Drop coalescence is one of the processes that is responsible for the evolution of drop sizes and without coalescence, real steady state could not be achieved. The relative motion between drops result in collisions which lead to coalescence. Coalescence is more complex compared to breakage as the interactions between drop and surrounding liquid as well as the interactions between drops have to be considered. It occurs when two drops which are suspended in moving fluid, collide and combine into larger drops. It involves drainage and rupture of the intervening liquid film between the contacted drops, which is influenced by the physical properties and interface of the liquids. The film drainage concept is a common theory used in modeling of coalescence process apart from other theories but in all cases, contact and collision between drops are the essence of coalescence process.

The number of collisions between drops influences the coalescence rate which is induced by impacts such as collisions with impeller blades, baffles, and vessel walls. However, not all collisions result in coalescence as it have to meet several requirements such as having sufficient energy and contact time which will be discussed in the modeling of coalescence kernels. Therefore, the concept of coalescence efficiency is used where coalescence rate model is developed as a product of collision frequency, \( h(d_c, d) \) and coalescence efficiency \( \lambda(d_c, d) \).

Semiempirical Correlations

Numerous parametric studies on mean drop size have promoted the development of predictive empirical correlations of Sauter mean diameter, \( d_{32} \). Most of the correlations have been developed from the prediction of maximum drop diameter, \( d_{\text{max}} \) based on the Hinze–Kolmogrov concept of turbulent energy cascade. Most correlations are derived for a stationary state but sometimes additional provision is taken to include the transient drop size.

Relationship between Sauter mean diameter and maximum drop diameter

Earlier studies have proposed that \( d_{\text{max}} \) is related to \( d_{32} \) \( (d_{32} \approx d_{\text{max}}) \) in the case where drop size is controlled by breakage. However, Sprow (1967) assumed that \( d_{32} \) was proportional to \( d_{\text{max}} \) \( (d_{32} \propto d_{\text{max}}) \) and pioneered the studies on the linear relationship between \( d_{32} \) and \( d_{\text{max}} \) by introducing the proportional constant, \( C \) based on \( d_{32} = Cd_{\text{max}} \). The proportional relation has been applied by most researchers to develop semiempirical \( d_{32} \) correlations. The work to investigate the relation between \( d_{32} \) and \( d_{\text{max}} \) has been extended for different conditions where values of constant \( C \) at different conditions range between 0.38 and 0.70 as summarized by Zhou and Kresta (1997). However, the authors did not support the linear proportional relation between \( d_{32} \) and \( d_{\text{max}} \). According to their work, the relationship was nonlinear but with insignificant change over a limited range of impeller speed, \( N \) where \( k \) decreases with increase in \( N \) and was supported by Sechremeli et al. (2006).22

Mean drop size correlation for breakage dominating system

Based on the drop breakage mechanism in turbulent flows, drop with diameter \( d \) is opposed by disruptive energy from
In Eq.4, \( E(k) \) is the energy spectral density function and \( k \) is the wave number or inverse eddy length. Only eddies with scale smaller than \( k=1/d \) are considered because it was assumed that only eddies equal or smaller than the drop diameter can cause drop breakage. According to Kolmogrov theory of local isotropy, if the drop diameter is smaller than the value of turbulence macro-scale and larger than the value of Kolmogrov microscale \((L>>d>>\eta)\), \( \tilde{u}^2(d) \) is mainly a function of local energy dissipation rate, \( \varepsilon \). Assuming that drop sizes in stirred vessels fall within the inertial subrange, \( E(k) \) is estimated as below

\[
E(k) = \beta_k c^{2/3} k^{-5/3}
\]

Therefore, \( \tau_c \) is related to \( \varepsilon \) as

\[
\tau_c = \rho_c \varepsilon^{2/3} d^{2/3}
\]

Drop’s cohesive forces consist of surface force per unit area, \( \tau_s \) and internal viscous stress, \( \tau_d \) are estimated as \( s^{33} \)

\[
\tau_s = \frac{\sigma}{d}
\]

\[
\tau_d = \mu_d \left( \frac{\varepsilon}{c} \right)^{1/2}
\]

A drop can only be broken if the disruptive forces acting on the drop is larger than the combined cohesive forces of the drop. Therefore, when the disruptive force is equally balanced by the cohesive stresses, drop with a maximum size, \( d_{\text{max}} \) is formed. Therefore, \( d = d_{\text{max}} \) exists when

\[
\tau_c = \tau_s + \tau_d
\]

Substituting Eq. 6–8 into Eq. 9

\[
\rho_c \varepsilon_{\text{max}}^{2/3} d_{\text{max}}^{2/3} = \frac{\sigma}{d_{\text{max}}} + \mu_d \left( \frac{\varepsilon}{c} \right)^{1/2}
\]

In Eq. 10, \( \varepsilon_{\text{max}} \) is used instead of \( \varepsilon \) as \( d_{\text{max}} \) is determined by the maximum energy region of the flow. Thus, rearranging Eq.10 for \( d_{\text{max}} \)

\[
d_{\text{max}} = \left( \frac{\sigma}{\rho_c \varepsilon_{\text{max}}^{2/3}} \right)^{3/5} + \left( \frac{\mu_d}{\rho_c \varepsilon_{\text{max}}^{2/3}} \right)^{1/2}
\]

Based on Eq. 11, \( d_{\text{max}} \) is controlled by surface tension and viscous force. If the dispersed phase viscosity is small, that is, inviscid drop, the viscosity term in Eq.11 is smaller compared to surface force and thus can be neglected. In this case, drop resistance against breakage is only contributed by surface force. Hence, Eq. 11 becomes

\[
d_{\text{max}} = C_1 \left( \frac{\sigma}{\rho_c} \right)^{3/5} \varepsilon_{\text{max}}^{-2/5}
\]

In the case of fully developed turbulence, \( \varepsilon_{\text{max}} \) is estimated by the relation of \( \varepsilon_{\text{max}} \propto N^3 D^5 \) for dispersion with a turbine agitator in a fully baffled tank and at a constant power number regime. Therefore, Eq. 12 becomes

\[
\frac{d_{\text{max}}}{D} = C_2 \left( \frac{\rho_c N^3 D^5}{\sigma} \right)^{-3/5}
\]

Equation 13 can be written as

\[
\frac{d_{\text{max}}}{D} = C_2 \text{We}^{-0.6}
\]

where We is a dimensionless group called Weber number, which represents the ratio of disruptive force to cohesive force (surface force) as

\[
\text{We} = \frac{\rho_c N^3 D^5}{\sigma}
\]

According to the proportional relation between \( d_{\text{max}} \) and \( d_{32} \), Eq. 15 is related to \( d_{32} \) by

\[
\frac{d_{32}}{D} = C_3 \text{We}^{-0.6}
\]

Equation 16 is the general empirical equation relating mean drop size to We. The equation is independent of geometry of mixing devices but the value of constant \( C_3 \) depends on stirrer types and has to be determined experimentally. The values reported in literature are between 0.38 and 0.70\( ^{35} \). The equation only considered pure breakage system with resistance to deformation by surface force only. As a result, the empirical equation is bounded to a narrow range of operating conditions where it is only valid for dispersed phase fraction below \( \phi = 0.01 \) making Eq. 6 to be the most popular functional form used to correlate drop sizes in dilute and inviscid systems.\(^{36} \)

However, not all data are well correlated by the empirical equation and, therefore, several modifications have been made on the values of the We exponent. Baldyga et al., (2001)\(^{37} \) proposed that there were significant limitations in the classical drop size correlations which were based on the time-averaged rate of turbulent energy dissipation. The We exponents obtained in their experimental work (−0.59 to −0.79) fell well below −0.6. Therefore, semiempirical model were developed by determining the exponential values based on the experimental data in their work.

### Mean drop size correlations for breakage and coalescence system

Mean drop size correlation as in the form of Eq. 6 is not applicable for systems with significant coalescence. The limitation of Eq. 6 has been observed for concentrated systems where the dispersed phase fraction, \( \phi \) is high. As \( \phi \) increases, the rate of drop breakage reduces and larger \( d_{32} \) are produced. Desnoyer et al., (2003)\(^{25} \) reported that drop breakage mechanism was modified at high phase fraction based on the author’s investigation on \( \phi \) values up to 0.6. Increase in \( d_{32} \) values as \( \phi \) increased was reported to be attributed by turbulence dampening or mainly by the occurrence of drop coalescence. However, several researchers believe that both factors are equally responsible for the observed trends.\(^{38} \)

Increase in dispersed phase fraction indicates the existence of higher drop population density in the continuous phase which can reduce the turbulent energy available to disrupt the drop by affecting the local energy dissipation rate as
discussed by Doulah (1975). Higher drops population also increases the frequency of drop collisions, contributing to high coalescence rate. Therefore, the assumptions that drop sizes are produced by drop breakage only may be not suitable for a system with high $\phi$.

To account for the increase in mean drop size as the dispersed phase fraction increase, Doulah$^{39}$ shows that the mean drop size at high phase ratio could be correlated empirically by adding correction factor to $d_{32}$ for dilute case as in the following equation

$$d_{32} = (1 + C_4 \phi) d_{32} \quad (17)$$

Doulah$^{39}$ showed that the value of $C_4$ was equal to 3 for breakup dominated system with negligible coalescence. Even for noncoalescence system, $d_{32}$ was found to still depend strongly on the dispersed phase fraction as reported by Maas et al., (2012).$^4$ Hence, it proved the effects of turbulence dampening on $d_{32}$ as dispersed phase fraction increased. The correction factor which is a linear function of hold-up fraction, $\phi$, is added in the Weber number relation to account for possible coalescence. The constant $C_3$ in Eq. 16 can be altered to include the correction factor as

$$C_4 = C_3 (1 + C_4 \phi) \quad (18)$$

Thus, the mean drop size model is modified to include the effects of coalescence at high phase ratio

$$\frac{d_{32}}{D} = C_5 (1 + C_4 \phi) We^{-0.6} \quad (19)$$

In Eq. 19, two constants are introduced where both constants depend on the studied system and thus have to be determined experimentally. The constant $C_5$ depends on stirrer types while $C_4$ depends on the tendency for the drop to coalesce.$^{38}$ Therefore, $C_4$ is influenced by the properties of the liquids studied and can be used as an indicator for occurrence of coalescence in the system.$^1$ The values of $C_4$ reported in the literature range from 3 to 20 which represent the strength or effectiveness of drop coalescence process on drop size evolution.$^{35}$ When $C_4 = 3$, it indicates the occurrence of turbulence dampening in the vessel while a value of $3 < C_4 < 10$ indicates the occurrence of coalescence.$^1$ When $C_4 > 10$, it is strongly coalesced system where coalescence might be the dominating process.

Table 1 shows the examples of models based on the form of Eq. 19 with the information on the system properties. From the table, constants with different values were observed in each of the proposed models, which show that the models are highly system specific.

**Mean drop size correlations for high viscosity system**

Most studies on liquid–liquid dispersion have focused on nonviscous dispersed phase where the effect of internal viscous force on resistant to drop breakage is negligible. Thus the developed correlations are limited to drop stabilization by surface force only. However, if the viscous force is larger compared to the surface force such as in the case of high $\mu$, the contribution of viscous force should be considered.$^{11}$ Increase in viscous forces means higher resistance to drop breakage as the cohesive forces is increased. As a result, low viscosity liquids approaches equilibrium $d_{32}$ faster than viscous liquids where less agitation time is required at low viscosity.$^{42}$

---

**Table 1. Mean Drop Size Correlations Based on Drop Breakup and Coalescence**

<table>
<thead>
<tr>
<th>Authors</th>
<th>Correlations</th>
<th>Phase Fraction, $\phi$</th>
<th>Liquid Properties $(\mu = \text{mPas}, \sigma = \text{mNm}^{-1})$</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pacek and Nienow, (1998)$^{28}$</td>
<td>$\frac{d_{32}}{D} = 0.022(1 + 23.3\phi) We^{-0.43}$</td>
<td>0.005–0.1</td>
<td>Chlorobenzene/Water $\mu = 1, \sigma = 33.4$</td>
<td>6-blade disk turbine</td>
</tr>
<tr>
<td>Quadros and Baptista (2003)$^{20}$</td>
<td>$\frac{d_{32}}{D} = 0.0336(1 + 13.76\phi) We^{-0.6}$</td>
<td>0.06–0.166</td>
<td>Chlorobenzene/NaCl $\mu = 1, \sigma = 33.8$</td>
<td>2-paddle impeller.</td>
</tr>
<tr>
<td>Desnoyer et al. (2003)$^{25}$</td>
<td>$\frac{d_{32}}{D} = 0.0286(1 + 13.24\phi) We^{-0.6}$</td>
<td>0.1–0.6</td>
<td>Disisobutylene/Benzene $\alpha = 16.35, 34°C \pm 0.5°C$</td>
<td>4-paddle impeller.</td>
</tr>
<tr>
<td>Jahanzad et al. (2005)$^1$</td>
<td>$\frac{d_{32}}{D} = 0.022(1 + 3.55\phi) We^{-0.6}$</td>
<td>0.05–0.4</td>
<td>Noncoalescing system, HCl, $\mu = 1.068, \alpha = 10$</td>
<td>4-blade flat turbine.</td>
</tr>
<tr>
<td>Singh et al. (2008)$^{36}$</td>
<td>$\frac{d_{32}}{D} = 0.005(1 + 0.32\phi) We^{0.6}$</td>
<td>0.2–0.5</td>
<td>MMA and styrene in water + PVA and LPO, 70°C $\pm 0.5°C$</td>
<td>4-trapezoid blade top shrouded turbine.</td>
</tr>
<tr>
<td>Razzaghi and Shahrazi, (2010)$^{18}$</td>
<td>$\frac{d_{32}}{D} = 0.084(1 + 0.9\phi) We^{-0.6}$</td>
<td>0.005–0.1</td>
<td>Organic (N-paraffin, D2EHPA, TBP) $\mu = 4.01, \sigma = 26.7$</td>
<td>25°C</td>
</tr>
<tr>
<td>Maaß et al. (2012)$^4$</td>
<td>$\frac{d_{32}}{D} = 0.246\exp(0.55\phi) We^{0.6}$</td>
<td>0.02–0.45</td>
<td>Aqueous (phosphoric acid) $\mu = 4.28, \sigma = 19.4$</td>
<td>Flat blade impeller.</td>
</tr>
</tbody>
</table>

**Phase Fraction, $\phi$, and Liquid Properties:**
- Chlorobenzene/Water: $\mu = 1$, $\sigma = 33.4$
- Chlorobenzene/NaCl: $\mu = 1$, $\sigma = 33.8$
- Disisobutylene/Benzene: $\alpha = 16.35$, $34°C \pm 0.5°C$
- Noncoalescing system, HCl: $\mu = 1.068$, $\alpha = 10$
- MMA and styrene in water + PVA and LPO, 70°C $\pm 0.5°C$
- Organic (N-paraffin, D2EHPA, TBP): $\mu = 4.01$, $\sigma = 26.7$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
- Aqueous (phosphoric acid): $\mu = 4.28$, $\sigma = 19.4$
Based on the observation on drop breakage by Hermann et al., (2011)33 using computational fluid dynamic (CFD) the authors reported that increase in viscosity caused less breakage events away from the stirrer blade and the drop breakage events ended earlier behind the stirrer blade. Drops with lower viscosity can be broken at regions far away behind the stirrer blades in the investigated region. Therefore, drop breakage probability is higher at low dispersed phase viscosity which leads to increase in drop breakage rate.

In the case of high $\mu_d$, the assumption of inviscid drop in deriving Eq. 16 is not valid. Therefore, the model should be extended to include the effect of $\mu_d$ in the correlation of $d_{32}$. In this condition, Eq. 10 becomes

$$\frac{d_{\text{max}}^{2/3}}{\sigma} = C_6 \left[ 1 + C_7 \left( \frac{\rho_s}{\rho_d} \right)^{1/2} \frac{\mu_d}{\sigma} \frac{V_i}{d_{\text{max}}^{1/3}} \right]$$

(20)

In Eq. 20 if $\mu_d$ is small, the right-hand term in the bracket becomes small with respect to unity and the surface force dominates the internal viscous force. However, in the case of high $\mu_d$ where the surface force, $\sigma$ is small, internal viscous force predominates and the right-hand term in the bracket becomes large with respect to unity. Therefore, Eq. 20 becomes

$$d_{\text{max}} = C_8 (\rho_s \rho_d)^{-3/8} \mu_d^{3/4} \max^{-1/4}$$

(21)

Equation 21 predicts the maximum drop size at high dispersed phase viscosity where the internal viscous force dominates the drops resistance against breakage. However, Wang and Calabrese (1986)31 discovered the dependency on interfacial tension even at high dispersed phase viscosity. Therefore, a dimensionless parameter called viscosity number, $V_i$ has been introduced to represent the effects of $\mu_d$. The viscosity number is a qualitative measurement of the relative importance for both $\sigma$ and $\mu_d$. To include both the influence of interfacial tension and dispersed phase viscosity, a semiaempirical approach has been proposed to develop various correlations for drops with wide range of viscosity as in the following equation 31

$$\frac{d_{32}}{D} = C_8 V_i^{-0.6} \left[ 1 + C_9 V_i \left( \frac{d_{32}}{D} \right)^{1/3} \right]^{0.6}$$

(22)

$V_i$ represents the ratio of viscous to surface forces in drop stabilization. The parameter shows qualitative measure on the relative importance of both forces in drops stabilization. It is written as

$$V_i = \left( \frac{\rho_s}{\rho_d} \right)^{0.5} \frac{\mu_d}{\sigma}$$

(23)

Wang and Calabrese 31 then simplified the semiempirical model to the following form

$$\frac{d_{32}}{D} = C_8 V_i^{-0.6} [1 + C_9 V_i^{0.6}]$$

(24)

For inviscid drops ($\mu_d \approx 0$), Eq. 24 will revert back to Eq. 16. Table 2 shows the examples of drop size correlations which relate $d_{32}$ to $\mu_d$.

### Table 2. Models on Mean Drop Size for High Viscosity

<table>
<thead>
<tr>
<th>References</th>
<th>Correlations</th>
<th>Viscosity, $\mu_d$ (mPas)</th>
<th>Phase Fraction, $\phi$</th>
<th>Liquid Properties</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wang and Calabrese (1986)</td>
<td>$d_{32} = 0.066 \left( 1 + 13.8V_i^{0.82} (\frac{\mu_d}{\sigma})^{0.31} \right)^{1/3}$</td>
<td>1–10000</td>
<td>0.002</td>
<td>Silicone Oil/Water/Methanol, $\sigma = 0.81$</td>
<td>Flat blade impeller, 25°C</td>
</tr>
<tr>
<td>Calabrese et al. (1986)</td>
<td>$d_{32} = 0.054 (1 + 3 \phi) V_i^{0.6} \left[ 1 + 4.42 (1 - 2.5 \phi) V_i \right]^{0.6}$</td>
<td>–</td>
<td>–</td>
<td>Used data from Calabrese et al. (1986) and Wang and Calabrese (1986)</td>
<td>–</td>
</tr>
<tr>
<td>El-Hamouz et al. (2009)</td>
<td>$d_{32} = 4.47V_i^{0.46}$</td>
<td>0.5–340</td>
<td>0.01</td>
<td>Silicone Oil/Water/SLES, High Shear tooth impeller and Pitch blade turbine</td>
<td>–</td>
</tr>
<tr>
<td>Khakpay and Abolgahsemi (2010)</td>
<td>$d_{32} = 0.172 (1 + 23.6 \phi) \left[ 1 + 2880 (\frac{\mu_d}{\sigma})^{0.82} \right] V_i^{-0.59}$</td>
<td>0.7</td>
<td>0.1–0.721</td>
<td>Butyl acetate/Water, $\sigma = 12.9$ mNm$^{-1}$</td>
<td>Spiral type impeller, 25°C</td>
</tr>
<tr>
<td>Zainal Abidin et al. (2014)</td>
<td>$d_{32} = 1.588V_i^{-0.53} \left[ 1 + 0.0227V_i^{1.4} \right]$</td>
<td>20–500</td>
<td>0.01</td>
<td>Silicone oil/SDS, $\sigma = 17–18.9$ mNm$^{-1}$</td>
<td>Rushton turbine, 25°C</td>
</tr>
</tbody>
</table>

**Population Balance Equation**

PBE is the most common approach to simulate the operation of liquid-liquid dispersion. It has the advantage of allowing the description of breakage and coalescence processes in terms of identifiable physical parameters and operational conditions. Thus it is used to determine specific information such as drop breakage or coalescence frequency, coalescence efficiency and daughter size distribution based on the analysis of transient drop size.11 This approach allows description of dispersed phase by the means of a density function.47 It consists of a set of mathematical equations which is solved by numerical methods or statistical simulations. PBE is developed based on influent and effluent of drop into a control volume by “birth” and “death” of drops. The general form for a flow system is given as

$$\frac{\partial f(V_i,t)}{\partial t} + \nabla \cdot [n(V_i,t) \cdot n(V_i,t)] + \frac{\partial}{\partial V} \left[ \frac{\partial}{\partial V} f(V_i,t) \right] = -B(V_i,t) + D(V_i,t)$$

(25)

In Eq. 25, $B(V_i,t)$ is the birth rate of a drop while $D(V_i,t)$ is the death rate. For a perfectly agitated batch and insoluble system, the PBE can be represented as a univariate PBE that only account for individuals size change as shown in Eq. 26

$$\frac{\partial f(V_i,t)}{\partial t} = B(V_i,t) - D_b(V_i,t) + B_c(V_i,t) - D_c(V_i,t)$$

(26)
respectively. Each term in Eq. 26 represents discontinuous processes represented by submodels derived from mechanism theory.\textsuperscript{[49]}

\[
B_b(V, t) = \int_{V_p}^{V_{\text{max}}} v(V'\beta(V', V')g(V')f(V', t)dV'
\]

\[
D_b(V, t) = g(V)f(V, t)
\]

\[
B_c(V, t) = \frac{1}{2} \int_0^V h(V-V', V') \lambda(V-V', V')f(V-V', t)f(V', t)dV'
\]

\[
D_c(V, t) = f(V, t) \int_0^{V_{\text{max}}} h(V, V') \lambda(V, V')f(V', V', t)dV'
\]

The submodels $\beta(V, V')$ represent size distribution of daughter droplets formed after breakage of drop with volume $V'$, $g(V')$ is the breakage frequency, $v(V')$ is the mean number of daughter droplets after breakage of drop with volume $V'$, $h(V, V')$ is the collision frequency and $\lambda(V, V')$ is the coalescence efficiency between drop with volume $V$ and $V'$. For a practically effective simulation by PBE, it requires the determination of breakage and coalescence functions as the PBE submodels. Therefore, the challenge associated with the use of PBE is the identification of breakage and coalescence kernels that can accurately describe the actual dispersion process in turbulent flows in details.\textsuperscript{[38]}

The PBE can be further simplified depending on the system behavior such as for breakage or coalescence dominating system and can be transformed from the volume based form into drop diameter based function, $d$.

**Breakage frequency models**

Breakage frequency models, $g(d)$ in turbulent flows are derived based on the mechanism where drops are broken by the turbulent pressure fluctuations. Most models are based on assumptions that there is no relative mean velocity difference between the dispersed and continuous phase. Based on the mechanisms, breakage frequency models are developed based on the analysis of the process leading to drop breakage. Therefore, various models are available according to different assumptions made to describe the drop breakage process.

**Turbulent Kinetic Energy Greater than Critical Energy**

Coulaloglou and Tavlarides (1977)\textsuperscript{[48]} proposed phenomenological breakage frequency models based on the turbulent kinetic energy transmitted from drop-eddy collisions and a minimum energy value required to overcome the drops surface energy with the breakage time. In this process, oscillating drop will break if the kinetic energy transmitted to it is higher than the surface energy. The general form of the model is written as

\[
g(d_p) = \left(\frac{1}{\text{breakup time}}\right) \exp \left(-\frac{E_c}{E_k}\right)
\]

Assuming binary breakage which results to daughter drops with equal diameter, the breakage time, $t_b$ is defined as the time taken for a drop to undergo breakage and is given by eddy turnover time as\textsuperscript{[30]}

\[
t_b = \frac{d_p^{2/3}}{e_{\text{eddy}}^{1/3}}
\]

For resistance against breakage by surface force only, the energy fraction term in Eq. 31 is defined as the probability for breakage to occur and can be written as

\[
-\frac{E_c}{E_k} = \exp \left(-\frac{C_{2b}\sigma}{\rho d_p^{2/3}}\right)
\]

Similar to the development of semiempirical equation, correction factor $(1 + \phi)$ can be added into the model to consider the effects of turbulent dampening as dispersed phase fraction increases. Thus the following breakage frequency model is obtained by substituting Eqs. 32 and 33 into Eq. 31 with the addition of the correction factor

\[
g(d_p) = \frac{C_{1b}d_p^{1/3}}{(1 + \phi)d_p^{2/3}} \exp \left(-\frac{C_{2b}(1 + \phi)^2}{\rho d_p^{2/3}}\right)
\]

The model predicts a maximum in drop breakage frequency as the drop diameter increases or also called as non-monotonous behavior, resulting in higher stability to larger drops. The idea is to use the breakage time to determine the breakage rate where once the diameter reaches a certain size, breakage rate is affected by breakage time and the rate will decreases.\textsuperscript{[35]} There has been argument on the appropriateness of the behavior in modeling of breakage frequency. This has led to the development of other class of monotonous models in which the breakage frequency increases monotonously with increasing drop diameter. However, it has been reported recently that experimental data clearly shows a maximum for breakage frequency which response to large decrease of inverse breakage time as the parent drop diameter increases, which is in agreement with the nonmonotonous model prediction.\textsuperscript{[39]}

**Velocity Fluctuations Across Drop’s Surface.** Narsimhan and Gupta (1979)\textsuperscript{[51]} proposed that drop oscillation and breakage was induced by the difference in velocity fluctuations around the drop’s surface which was caused by eddies with different scales. The arguments led to development of another model class in the following functional form where the stoichiastic model is based on Poisson process

\[
g(d) = n \times \frac{1}{2} \text{erfc} \left(\frac{d_p}{\sigma \sqrt{2}}\right)
\]

where $n$ is the average number of eddies per unit time around drop’s surface. By the probability theory and assuming that the internal viscous force is negligible, the breakage frequency model is written as

\[
g(d) = c_{1b} \text{erfc} \left(\frac{\sigma}{e_{\text{eddy}}^{1/3}d_p^{2/3}}\right)
\]

The constants $c_{1b}$ and $C_{2b}$ in Eqs. 34 and 36 are adjustable model parameters and have to be determined empirically by fitting of experimental data.

**Eddy Energy Greater than Critical Energy.** The concept used to develop models in this category is that a drop can be broken if it hits eddies which contain energy greater than the drops critical energy to breakage, $E_c$. This kinetic theory-type model is based on the product of collision frequency, $\omega$ and breakage probability, $P$
This type of models is developed based on theoretical considerations. Thus it does not rely on empirical parameters. The critical energy for breakage, \( E_c \), is determined by various breakage criterions. The proposed criterions are based on the same breakage mechanism but according to different assumptions on how breakage occurs. Surface energy criterions represent the main process for breakage making it is one of the important criterions and has been widely used by many authors. Improved breakage criterions have been proposed based on extension of surface energy criterion or combination with other breakage criterions to take into account various parameters that influence drop breakage. Most of models proposed are well applied but only in the range of operating conditions based on the assumptions made during the model design and development. Therefore, promising models are developed without restricting assumptions so that it is applicable in various systems such as recent models by Han et al., (2014)\(^{53}\) and Ghasempour et al., (2014)\(^{54}\) which include wide energy spectrum.

**Surface energy criterion**

Luo and Svendsen (1996)\(^{16}\) proposed collision frequency and breakage probability in the form

\[
\omega_{\text{collision}}(d, \lambda) = \frac{7}{4} (d + \lambda)^2 \tilde{u}_d \cdot 0.822(1 - \phi)/\lambda^4
\]

\[
P(d) = \exp(\lambda_c) = \exp[E_c(d)/\tilde{E}(\lambda)]
\]

The breakage probability, \( P(d) \), is determined by energy criterion in which Luo and Svendsen\(^{16}\) have used surface energy criterion as a constraint for drop breakage to occur. This criterion has been widely applied by many authors with several modifications. According to the criterion, droplet breakage occurs when colliding eddies contain enough turbulent kinetic energy to compensate for the increase in surface energy in droplets after the droplet broken into smaller drops, that is, \( E_c(\lambda) \geq e_c(d, d') \). Thus, assuming binary breakage into equal size daughter drops, \( E_c(d) \) is written as

\[
E_c(d) = \pi \sigma (d^2 + (d^3 - d'^3)^{2/3} - d^2)
\]

In the inertial subrange, the mean turbulent kinetic energy of eddies, \( \tilde{E}(\lambda) \), is given as

\[
\tilde{E}(\lambda) = \frac{\pi \beta \rho \lambda^2}{12} \lambda^{11/3}
\]

Thus, the breakage frequency given by Luo and Svendsen\(^{16}\) in dimensionless form is given as

\[
g(d) = \frac{0.923}{2} (1 - \phi) \left( \frac{\lambda}{2} \right)^{1/3} \int_{\xi_{\text{min}}}^{1} \left( 1 + \xi^2 \right)^{7/6} \exp \left( - \frac{12 e_c \sigma}{C_s \rho \lambda^2 / \lambda_{\text{mix}}^{11/3} } \right) d\xi
\]

In Eq. 42, the upper integration limit of 1 (\( \xi = \lambda/d \)) indicates that drop breakage is only caused by turbulent eddies which are less than and equal to the size of drops. This model is a monotonous model that does not predict a maximum breakage frequency. The advantage of this model is that it does not contain any adjustable model parameter as in the previous models but the result depends strongly on the choice of integration limit. The lower integration limit has low to moderate effects while the upper integration limit has very high effects on the total breakage frequency. This model was successfully applied recently by Srilatha et al. (2010).\(^{55}\)

The surface energy criterion proposed by Luo and Svendsen\(^{16}\), however, causes inherent inconsistency as it does not have lower limit for drop sizes. Therefore, the breakage rates for very small drop particles are also included in the theory resulting in very high total breakage rate.

**Energy density criterion**

To overcome the weakness, Hagesaether et al., (2002)\(^{56}\) expanded and refined the model by Luo and Svendsen\(^{16}\) by proposing a new breakage criterion called energy density criterion, which considers existence of a physical lower limit to the drop size being broken. According to this criterion, in order for drop breakage to occur, the eddy should have energy density higher or equal to the energy density of the daughter drops which are produced by the breakage. The lower limit is determined from the surface energy density, \( w_c(d) \) for a smallest daughter drop

\[
w_c(d) = \frac{4 \pi (d/2)^2 \sigma}{(4/3) \pi (d/2)^3}
\]

The energy density probability function, \( P_c(d) \) is written as a normalized function

\[
P_c(d) = \frac{w_c(\lambda) - 6 \sigma / d_k}{\int_{d_{k_{\text{min}}}}^{d_{k_{\text{max}}}} w_c(\lambda) - 6 \sigma / d_k d(d_k)}
\]

where \( d_k \) is the possible smallest daughter particle and \( w_c(\lambda) \) is the eddy energy density

\[
w_c(\lambda) = \frac{e_c(\lambda)}{(4/3) \pi (\lambda/2)^3}
\]

The energy density criterion is used with surface energy criterion, where the surface energy probability, \( P_s \) can also be written as a normalized function

\[
P_s(d, d') = \frac{e_c(\lambda) - e_i(d, d')}{\int_{0}^{0} e_c(\lambda) - e_i(d, d') d(d)}
\]

The breakage probability by surface energy criterion and energy density criterion are combined into total breakage probability as

\[
P_b = P_c P_d
\]

Hagesaether et al., (2002)\(^{56}\) defined the critical breakage point and the critical energy for breakage as

\[
e_c(\lambda)_{\text{CBP}} = e_c(d, d_{k_{\text{min}}})
\]

In Eq. 48, \( d_{k_{\text{min}}} \) is the lower limit diameter due to energy density criteria. The breakage probability, \( P_b \) is determined as

\[
P_b = \int_{x_c}^{\infty} \exp(-x) dx = \exp(-x_c)
\]

where \( x_c = e_c(\lambda)_{\text{CBP}} / \tilde{E}(\lambda) \).

**Stress criterion**

Based on the work by Andersson and Andersson (2006)\(^{57}\) on the breakage of single fluid particle, drop often deform
significantly before breaking into smaller fragments. Based on the finding, physical criterions for drop breakage to determine the breakage probability, $P_b$ were introduced which are energy and stress criterion in their separate work, Andersson and Andersson (2006).\(^5\) Using the criterions, breakage rate does not depend on the selection of upper and lower integration limit anymore.

Andersson used the concept of interaction frequency, $\omega_{interaction}$ instead of collision frequency, $\omega_{collision}$ in Luo and Svendsen\(^1\) model. They proposed that the interaction frequency was proportional to volume of drop particle and high energy eddy might cause one breakage during its turnover time. Therefore, the interaction frequency is written as

$$\omega_{interaction}(d_0, \lambda) = \frac{C_A \pi (1 - \phi) d_0^3 d_p^{5/3} n_k}{6 \lambda^{14/3}}$$  (50)

where $d_0$ is the parent drop. Based on the energy and stress criterions, in order for drop breakage to occur, eddy should contains enough energy that exceed the increase in interfacial energy and the disruptive turbulent stress should exceeds the cohesive interfacial stress. The breakage criterion based on the interfacial energy is given by

$$\epsilon_{interfacial\ energy}(d_p) \geq \sigma \pi d_p^2 \lambda$$  (51)

while the stress criterion is given by

$$\rho \mu \lambda^2 / 2 \geq 2\sigma / d$$  (52)

For very small eddies, although high in numbers, do not fulfill the stress and energy criteria while very large eddies, although it fulfill both criteria, it only have small contribution to the overall breakage rate as its number density is very low. Therefore, this model is not sensitive to the selection of upper and lower integration limit.

**Breakage by larger eddies criterion**

Traditionally, it is assumed that only eddies equal to or smaller than drop size would cause drop breakage while larger eddies only cause translation (except for breakage models proposed by Hagesaether et al.\(^5\) and Andersson\(^8\)). However, according to the work by Andersson and Andersson,\(^9\) drop stretched significantly before splitting into smaller daughter drop in which smaller eddies were not capable of performing the large scale deformations. Andersson reported that their proposed model, drop breakage is caused by eddies whose size is approximately equal to and up to three times larger than the drop size. Considering the experimental observations, Han et al., (2011)\(^9\) proposed a mechanism for drop breakage by larger eddies, where larger eddies can partially transfer energy to the drop causing change in velocity at different position of the drop. The author suggested that constraints imposed for drop breakage by larger eddies should be different from that of equal or smaller eddies.

**Eddies Equal or Smaller than Drop Diameter.** In this case, Han et al., (2011)\(^9\) proposed a breakage constraint and a collision frequency model. A constraint was proposed with an assumption that eddy kinetic energy was fully utilized by the deformed drop with clean surface

$$\epsilon(\lambda) \geq \pi d_0^2 \sigma \left( \frac{1}{d_{14}^{1/3}} - 1 \right)$$  (53)

With $f_{14} = (d_1 / d_0)$ and $d_1$ being the diameter of the smallest fragments. Combining the constraint with the surface energy increase constraint, a criterion for drop breakage is obtained as

$$\epsilon(\lambda) \geq \max(c_1, c_3) \pi d_0^2 \sigma$$  (54)

where $c_1 = f_{14}^{2/3} + (1 - f_{14})^{2/3}$, $c_3 = \min(f_1, 1 - f_1)^{-1/3} - 1$, and $f_1 = (d_1 / d_0)^{1/3}$. To develop a collision frequency model, Han et al., (2011)\(^9\) consider that surface oscillation of a drop from previous collision with eddies containing energy might not disappear completely before the next collision. Therefore, the drop might probably contain a part of energy which could contribute to the total energy in the next breakage. Assuming that the surface oscillation obeys a sinusoidal function and by introducing a dimensionless oscillation ratio, $C_0$ a collision frequency model is written as

$$\omega_{collision}(d_0, \lambda) \approx 0.923(1 - \phi) n_k^{1/3} (1 + C_0 + x)^2 x^{-11/3} d_0^{5/3}$$  (55)

where $x = \lambda / d_0$ and $\lambda \leq d_0$.

**Eddies Larger than Drop Diameter.** For eddies larger than the drop size ($\lambda > d_0$), the available eddy energy, $\epsilon_{available}(\lambda)$ as discussed by Andersson\(^8\) should be less than $\epsilon(\lambda)$. Thus, Han et al.,\(^9\) proposed a sinusoidal velocity distribution function ($u = A \sin(\pi \lambda / \lambda_0)$) where $y$ is the distance centroid of an eddy (ranges from 0 to $\lambda_0 / 2$) to estimate available eddy energy, $\epsilon_{available}(\lambda)$. The breakage constraint for ($\lambda > d_0$), is then written as

$$\epsilon(\lambda) \geq \frac{\max(c_1, c_3) \pi d_0^2 \sigma}{4(\lambda / d_0)^{1/3} \sin^2(\pi / 4\lambda / \lambda_0)}$$  (56)

For eddies larger than drop diameter, instead of collision frequency, an interaction frequency model was used by Han et al.,\(^9\) where the authors considered the effect of transport time in their model. They proposed that the transport time was shorter than eddy lifetime which means that a drop is transported across eddies before eddies disappear. Thus, they incorporated the transport time into the interaction frequency model by Andersson and Andersson\(^8\) as

$$\omega_{interaction}(d_p, \lambda) \approx \frac{0.43(1 - \phi) n_k^{1/3}}{\lambda^{14/3} d_0^{5/3} \min(1, 1 / 2 \sqrt{2} \sin^2(\pi / 4\lambda / \lambda_0))}$$  (57)

where $x = \lambda / d_0$ and $\lambda > d_0$.

**Multiple breakage criterions**

Most of the models discussed earlier are based on the assumption that a drop breaks into two daughter drops (binary breakage) which can greatly simplify the problems. In a recent work by Han et al., (2013),\(^6\) multiple breakage model (binary, ternary, and quaternary) was developed which relates the multiple breakage process to turbulence condition. The model was derived from their previous model which considers breakage by larger eddies.

A condition for breakage was proposed in which the energy density of parent drop obtained from turbulent eddy should be equal to or more than the maximum of all surface energy increases of daughter drops. The multiple breakage process was proposed as a series of binary breakage processes. For example, for a ternary breakage, a parent drop splits into two fragments, which are a daughter drop size $d_1$ and an intermediate drop with size $d_{10}$. The intermediate drop will again split into daughter drops with size $d_{2}$ and $d_{3}$. Based on surface energy density increase constraint, for
eddy size smaller than drop diameter, a modified energy criterion is given as
\[ e(\lambda) \geq \max(c_{1,n}, c_{2,n}) \pi d_0^2 \sigma \]  (58)
and for eddies larger than drop diameter, the energy criterion is
\[ e(\lambda) \geq \frac{\max(c_{1,n}, c_{2,n}) \pi d_0^2 \sigma}{4(\lambda/d_0)^3 \sin^4(\pi/4)(d_0/\lambda)} \]  (59)

The model is similar to their previous model but for multiple breakage, \( c_{1,n} \) and \( c_{2,n} \) are used instead of \( c_{1} \) and \( c_{2} \) to represent the series of breakage events. The functions are given as
\[ c_{1,n} = \left( \sum_{j=1}^{n} f_{i,j}^{3/2} \right)^{-1} \]  (60)

For binary, ternary and quaternary breakage
\[ c_{22} = \min \left[ f_{r,1}^{-1/3}, (1-f_{r,1})^{-1/3} \right] - 1 \]  (61)
\[ c_{23} = c_{22} + c_{1,3} \left\{ \min \left[ f_{r,2}^{-1/3}, (1-f_{r,1}-f_{r,2})^{-1/3} \right] - (1-f_{r,1})^{-1/3} \right\} \]  (62)
\[ c_{24} = c_{22} + c_{1,4} \left\{ \min \left[ f_{r,12}^{-1/3}, f_{r,13}^{-1/3} \right] - (1-f_{r,1})^{-1/3} \right\} + \min \left[ f_{r,3}^{-1/3}, f_{r,4}^{-1/3} \right] - f_{r,34}^{-1/3} \]  (63)
where \( f_{r,12} = 1 - f_{r,1} - f_{r,2}, f_{r,34} = f_{r,3} + f_{r,4}, \) and \( f_{r,4} = 1 - f_{r,1} - f_{r,2} - f_{r,3}. \)

**Energy spectrum model**

Most of the breakage kernel models discussed earlier assumed that parent drops in the system fall in the inertial subrange \((L > d > \eta)\) according to Kolmogrov length scale, \( \eta \) to estimate the turbulent fluctuation. Therefore, the minimum drop size is estimated by the Kolmogrov length scale, \( \eta \). In this case, the energy spectrum, \( E(k) = Bk\epsilon^{3/2}k^{-5/3} \), and the mean turbulent velocity, \( \bar{u}(\lambda) = C(\epsilon/\mu)^{1/3} \), are incorporated in their breakage model, where the turbulent velocity is independent of fluid viscosity.

However, eddies in the inertial subrange might not be always comparable to the drop size and thus the case might not be satisfied in every actual application. The use of Kolmogrov length scale to estimate minimum drop size is also considered as inappropriate especially when no coalescence is involved.\(^{12}\) Although small in number, drops with size below the length scale can be produced at high viscous shear forces region, that is, in impeller region. When drops are smaller than \( \eta \) (\( d < \eta \)), the independency of \( \bar{u} \) on fluid viscosity is no longer holds where \( \bar{u}(\lambda) = C(\epsilon/\mu)^{1/3} \lambda \). This regime is called as viscous subrange, and \( E(k) \) in this regime is different from the one in the inertial subrange. Therefore, models which are based on the inertial subrange might not be applicable for drops below the size of Kolmogrov length scale, although low in number.

To overcome the limitations, an improved model that considered wide energy spectrum was proposed in a recent work by Han et al., (2014).\(^{53}\) The turbulent velocity, \( \bar{u}_x \), number density of eddies, \( n_c \), and mean kinetic energy, \( \bar{e}_k \), are determined to be
\[ \bar{u}_x \propto \sqrt{k E(k)} \]  (64)
\[ n_c = 3(1-\phi)k^2/2\pi^2c_0^2 \]  (65)
\[ \bar{e}_k = \frac{2}{3} \pi^4 c_0^2 \rho_e (E(k)/k^2) \]  (66)

Assuming binary breakage, for breakage by smaller or equal size eddies, the breakage kernel are developed based on the constraint
\[ e_k \geq \max \left[ f_{r,-1/3}, (1-f_{r})^{-1/3} - 1 \right] \pi d_0^2 \sigma \]  (67)

Therefore, the breakage probability with function of energy spectrum, \( E(k) \), is obtained
\[ n = \frac{3\sigma}{2\pi^3 c_0^2 \rho_e} \left[ \max \left[ f_{r,-1/3}, (1-f_{r})^{-1/3} - 1 \right] \pi d_0^2 \sigma \right] \]  (68)

where \( x = kd_0 \). The collision frequency was modified by considering surface oscillation of droplets as discussed earlier and is written as
\[ \omega_{\text{collision}}(d_0, x) = \frac{3(1-\phi)n}{8\pi^3 c_o} \left[ (1+S_0) + \frac{2\pi}{x} \right]^2 \frac{x^{5/2}}{d_0^{1/2}} \sqrt{E(x/d_0)} \]  (69)

where \( S_0 = \sqrt{\pi c_o/2\sqrt{2}} (3\rho_d + 2\rho_e/3\sigma)^{1/2} \sqrt{E(\delta)}. \) For breakage by larger eddies, the modified constraint and the critical dimensionless energy are given as
\[ e_k \geq \max \left[ f_{r,-1/3}, (1-f_{r})^{-1/3} - 1 \right] \pi d_0^2 \sigma \]  (70)
\[ n_c = \frac{3\sigma}{32\pi^3 c_0^2 \rho_e} \left[ \max \left[ f_{r,-1/3}, (1-f_{r})^{-1/3} - 1 \right] \pi d_0^2 \sigma \right] \]  (71)

The interaction frequency, \( \omega_{\text{interaction}} \) is written as
\[ \omega_{\text{interaction}}(d_0, x) = \frac{(1-z_0)n}{8\pi^3 c_o d_0^{1/2}} x^{5/2} \max \left[ 1, \frac{4\pi}{x} \sin^2 \left( \frac{x}{2d_0} \right) \right] \sqrt{E(x/d_0)} \]  (72)

Comparisons between different energy spectrum functions conducted by Han et al., (2014)\(^{53}\) shows that the breakage frequency is strongly affected by the function. The energy spectrum model which was paired with spectrum model of Pope (2000)\(^{18}\) shows very good agreement with experimental data. Han et al., (2014)\(^{53}\) also compared the breakage frequency models of Coulaloglou and Tavlarides (1977),\(^{48}\) Luo and Svendsen (1996)\(^{16}\) and their energy spectrum model with experimental data obtained by Anderson and Asserson (2006)\(^{58}\) and Maaß and Kraume (2012).\(^{50}\) The results shows that the energy spectrum models gives very good estimation which are very close to both sets of experimental data compared to the models that are based on inertial subrange conditions which under estimated (Luo and Svendsen\(^{15}\) and overestimated (Coulaloglou and Tavlarides\(^{48}\)) the breakage frequency. The energy spectrum also produced nonmonotonous breakage frequency which was agreed by the experimental data of Maaß and Kraume (2012).\(^{50}\)
Recently, Ghasempour et al., (2014), the authors showed that the number density of eddies, \( n_e \), as in Eq. 65 is, however, only valid in the inertial subrange of energy spectrum. Based on their studies on the number density of eddies in dissipation, inertial, and energy containing subrange, a number density models for complete energy spectrum is proposed as

\[
n_e = 24C_{f1}f_n\lambda^{-4/C_{\varepsilon}}(2\pi)^{5/3} \tag{73}
\]

where \( f_n \) and \( f_\lambda \) are nondimensional functions to determine the shape of the energy containing and dissipation ranges in the energy spectrum. The new model for entire energy spectrum gives significant improvement in the prediction of number density of eddies.

**Breakage Frequency Model at High Viscosity.** Both Eqs. 34 and 36 do not consider the viscous effects of the drop in which the internal viscous force on drop resistance against breakage is assumed to be negligible. At high viscosity, the increase in internal viscous force of the drop cause it to stretch and form a thin liquid thread until it achieves a critical thickness before splitting, producing more drop fragments. Therefore, as viscosity increases, the breakage process shifts from drop bursting to stretching and the time taken for breakage also increases. To account for different breakage mechanisms in the breakage time model, Maass and Kraume (2012) proposed a relation for elongation-induced breakage time, \( t_{b,e} \), from elongation time, \( t_e \) and the critical thread diameter of the elongated drops, \( d_{crit} \) as a function of elongation rate and physical properties of the system as

\[
t_{b,e} = \frac{2}{\epsilon} \ln \left( \frac{d_{a0}^6/\mu_0}{\sigma C_{\epsilon, crit}} \right) \tag{74}
\]

In Eq. 74, \( d_{a0} \) is the initial drop diameter, and the function \( C_{\epsilon, crit} \) which puts the viscous forces of the drop under elongation with capillary forces is determined by \( C_{\epsilon, crit} = \mu_0/(\sigma w) \) where \( w \) is the characteristic velocity, \( w = id_{crit} \). The \( t_{b,e} \) is related to resident time, \( t_{res} \), in stirrer region where the elongation rates is high and to turbulent breakage time, and \( t_{b,turb} \) as shown in Eq. 75. The resident time equation was derived by Kumar et al. (1998) as a function of impeller speed \( N \) as \( t_{res} = C/N \). Therefore, the modified breakage time model with function of viscosity becomes

\[
t_{b,e} = \frac{t_{b,e}}{t_{res}} = C_{1,b} N \frac{2}{\epsilon} \ln \left( \frac{d_{a0}^6/\mu_0}{\sigma C_{\epsilon, crit}} \right) \frac{d^{2/3}}{\epsilon^{1/3}} \tag{75}
\]

Based on the modified breakage time, the extended breakage frequency model is

\[
g(d) = C_{1,b} \frac{E}{N} \left( \ln \frac{d_{a0}^6/\mu_0}{\sigma C_{\epsilon, crit}} \right)^{-1} \frac{d^{2/3}}{\epsilon^{1/3}} \exp \left( -\frac{-C_{2,b} \sigma(1+\phi)^2}{\rho d^{2/3}/d^{5/3}} \right) \tag{76}
\]

Another approach of breakage frequency model which includes the effect of viscosity was proposed by Chen et al., (1998). The author considered the contribution of internal viscous stress, \( \tau_i \), together with the surface energy in the critical energy required for breakage to occurs which led to the following expression for \( E_c \)

\[
E_c = \frac{4\pi}{3} \frac{d^3 \sigma + C_{2,b} \mu \phi \epsilon^{1/3}}{1+\phi} \tag{77}
\]

The authors also claimed that the breakage time predicted by Eq. 32 yielded a maximum in breakage frequency which is physically not realistic. Thus, the breakage time is assumed to be constant \((1/h) = C_{1,b} \). Therefore from this approach, the breakage frequency model is expressed as

\[
g(d) = C_{1,b} \exp \left( -\frac{C_{2,b} \sigma(1+\phi)^2}{\rho d^{2/3}/d^{5/3}} - C_{3,b} \frac{\mu \phi}{\rho d^{1/3}/d^{2/3}} \right) \tag{78}
\]

The breakage frequency model in the form of Eq. 78 was also modified by Alopauc et al., (2002) where the viscous energy was included in the energy balance to derive the equation and the authors also included the dependence of \( \epsilon \) for the eddy-collision term. The modified model is expressed as

\[
g(d) = C_{1,b} \frac{d^{1/3}}{\epsilon} \text{erfc} \left( \sqrt{\frac{C_{2,b} \sigma(1+\phi)^2}{\rho d^{2/3}/d^{5/3}} + C_{3,b} \frac{\mu \phi}{\rho d^{1/3}/d^{2/3}}} \right) \tag{79}
\]

The equation includes the effects of both viscous and surface forces on drop stabilization to consider the damping effect at high viscosity. It can also be extended to account for damping effect at high phase fraction by adding the correction term \((1+\phi) \) as

\[
g(d) = C_{1,b} \frac{d^{1/3}}{\epsilon} \text{erfc} \left( \sqrt{\frac{C_{2,b} \sigma(1+\phi)^2}{\rho d^{2/3}/d^{5/3}} + C_{3,b} \frac{\mu \phi}{\rho d^{1/3}/d^{2/3}}} \right) \tag{80}
\]

**Mean number of daughter drops**

The number of drop fragments formed could be estimated by developing empirical relations based on the experimental data or by simply giving a fixed value as in the case of binary breakage. The mean number of daughter drop, \( v(V) \) in Eq. 27 is substituted by the number of drop fragments produced after splitting of mother drop of size \( d \).

In reality, for liquid systems, a parent drop breaks into smaller fragments which include a satellite drop which is very small compared to the daughter drops. For low viscosity liquid, ternary breakage is the dominant case, in which two daughter drops and a satellite drop are formed while at high viscosity, the internal viscous force caused more daughter and satellite drops to be formed. Therefore, most authors assumed binary breakage at low viscosity which is less complex and neglected the formation of satellite drop. Thus, in this case, \( v(V) = 2 \) is specified in PBE. The assumption might not be too restrictive as it is possible that the use of rapid sequence of binary breakage events could simulate any number of breakage fragments from a parent drop provided that the flow is uniform throughout the process. Besides, it is assumed that the size of the daughter drops for binary breakage is equal. The assumption is shown to be acceptable by Maass and Kraume (2012) as the possible diameter variation between two unequal size and equal size daughter drops is low.

However, although satellite drop is small in diameter, it could affect the values of contact area as the number of satellite drop formed is very high. Therefore, existing models can still be improved to account for the formation of satellite drops. There is relation between the numbers of daughter drop with the diameter of parent drop. Maass et al., (2007) reported that values larger than 2 (binary) should be used if
the mean diameter of the investigated drop size is larger
than 1 mm.

**Drop size distribution model**

The size distribution model $\beta(d, d')$ is required to describe
the daughter DSD which is the product of drop breakage
event. The formulation of distribution models requires infor-
mation on the shape of probability density function and the
number of drop fragments formed after a breakage event. The
models are derived from statistical and phenomenologi-
cal approach based on the change in drop’s surface energy.

Based on statistical approach, normal distribution, beta
distribution and hybrid models have been developed. The
discrepancies between the models is by the tendency of the
model to predict larger or smaller probability of equal-size
breakage, the use of zero probability on extremely small
drop daughter and exactly equal breakage and the
dependency on energy dissipation rate. Most of the existing
model are based on the assumption of equal sized daughter
drops. Due to insufficient of experimental data, there is a
lack of number and volume conservative DSD functions that
consider multiple unequal-size breakage combinations of
equal and unequal sized daughter particles which are
required for many systems.

**Statistical Model.** Normal Distribution Model: Generally,
model developed based on statistical approach are built on
the assumption that the function is normally distributed. A
distribution model was proposed by Coulaloglou and Tavlar-
dides (1977)\textsuperscript{48} that assumed binary breakage and the truncated
normal distribution are written as

$$\beta(d, d') = \frac{2}{d^3} \exp \left[ -4.5 \left( \frac{2d^2 - d'^2}{d^6} \right)^2 \right]$$  (81)

The model gives maximum probability for breakup into
equal sized daughter drops in which the case was supported by
the experimental data of Andersson (2006)\textsuperscript{57} and Maaß
et al., (2007).\textsuperscript{64}

Beta Distribution Model: Beta distribution function is able
to fit wider range of data compared to truncated normal distri-
bution model which is a single parameter model.\textsuperscript{65} A
binary breakage and beta distribution model was proposed by
Hsia and Tavlarides (1983)\textsuperscript{66} as

$$\beta(d, d') = 90 \frac{d^2}{d^3} \left( \frac{d^3}{d^2} \right)^2 \left[ 1 - \frac{d^3}{d^2} \right]^2$$  (82)

The advantages of beta distribution over normal distribu-
tion is that it predicts zero probability for daughter drops
with size equal to parent drop and drops which is infinitely
small. Beta distribution model is also able to completely
account for the total volume of fragments within upper and
lower bounds of drop size. The characteristic was found to
be beneficial by Azizi and Taweel (2010)\textsuperscript{68} as their de-
developed algorithm to solve discretized PBE gave highly stable
solution under low, moderate and high shear rate conditions
(up to $\epsilon = 1000$ W kg\textsuperscript{-1}).

Wang et al., (2003)\textsuperscript{66} suggested that a daughter drop pdf
should satisfy several important requirements such that it
should integrate to unity, be mass conserving, contain no sin-
gularity points, drop to zero as ratio between daughter and
mother drop diameters goes to zero and to one, describe the
effect of relevant physical parameters and the mother drop
diameter should be the pdf variables. Zaccone et al.,(2007)\textsuperscript{69}
reported that the model developed by Diemer and Olson
(2002)\textsuperscript{70} which could be used for higher order breakage,
meet all the requirements where the model is in the form of

$$\beta(d, d') = 3B^{-1}(q, r) \left[ 1 - \left( \frac{d'}{d} \right)^3 \right]^{r-1} \left( \frac{d'}{d} \right)^{-3q-1}$$  (83)

In Eq. 83, the two free parameters in the model are defined as functions of a shape parameter, $q$ and mean number of drop fragments produced per breakup event, $r$ with $r=q(v-1)$. Based on their work, the author proposed that the parameter $q$ should be modeled as an empirical function of the underlying physical situation. Therefore, extension of the beta pdf model was proposed by inserting the relation of Weber number which is based on the Hinze–Kolmogrov
theory and the dependence on mother drop’s diameter. The parameter $q$ is written as

$$q = 2\frac{W}{\gamma} \left( \frac{d}{d_p} \right)^{\delta}$$  (84)

where $\gamma$ and $\delta$ should be determined experimentally while $\lambda$
is a proportional constant by interpolation based on Eq. 84.
The critical diameter, $d_e$ is defined as the maximum stable
diameter based on Hinze–Kolmogrov theory.

**Phenomenological Model.** In phenomenological approach,
algebraic expression is developed to relate empirical observa-
tions of phenomena to each other. Based on this approach,
the shapes of DSD for both bubble and drop are classified as
bell-shape, U-shape, and M-shape. The most popular phenom-
ological model for DSD is a bimodal U-shape distribution
proposed by Tsouris and Tavlarides et al (1994),\textsuperscript{71} with higher
probability density at low and high volume fraction. In this
approach, it is assumed that the DSD function is linearly
related to the energy required to break a drop. The density
function is given as

$$\beta(d, d') = \frac{E_{\text{min}} + E_{\text{max}} - E(d')}{E_{\text{min}} + E_{\text{max}} - E(d) \int_{0}^{d} [E_{\text{min}} + E_{\text{max}} - E(d')] \, dd'}$$  (85)

In Eq. 85, $E_{\text{min}}$ is the minimum energy required to pro-
duce the smallest and largest drops, $E_{\text{max}}$ is the energy
needed to produce two daughter drops with equal size and
$E(d')$ is the energy required to produce two daughter drops
with size $d'$ and $d-d'$. The difference between this model
and beta function model is that this model predicts the mini-
mum probability for equal-size breakage while beta function
model which gives maximum probability.\textsuperscript{66}

**Hybrid Model.** A hybrid model (combination of statisti-
cal and phenomenological approach) was proposed by
Konno et al. (1983).\textsuperscript{72} The model is based on the energy dis-
tribution between turbulent eddies of different scales. The
authors assumed that the kinetic energy of a given size eddy
is proportional to the probability of forming a daughter dro-
plet where the energy was estimated by Heisenberg energy
spectrum. The formation of daughter drops was further
assumed to be caused by the interaction between parent
drops and turbulent eddies of the same size.\textsuperscript{4} The beta func-
tion is given as

$$\beta(d, d') = ...$$
\[
\beta(d, d') = \frac{\Gamma(12)}{\Gamma(3)\Gamma(9)} \left( \frac{d'}{d} \right)^8 \left( 1 - \frac{d'}{d} \right)^2
\]  
(86)

where \( \Gamma \) is a gamma function.

For simplification, it is assumed that the size of the daughter drops is equal.

**Coalescence rate**

Coalescence rate is formulated as the product of collision frequency between drops, \( h(d, d') \) and collision efficiency, \( \lambda(d, d') \) for drops with size \( d \) and \( d' \). Various collision efficiency models have been developed based on different mechanisms which are film drainage, energy, and critical approach velocity.

**Collision Frequency Model.** Mechanisms of drop collisions in stirred vessel include turbulent interactions between continuous and dispersed phase, buoyancy-driven collisions due to difference in rise velocities and collisions due to laminar shear.\(^{73}\) However, the dominant mechanism in turbulent flow is the turbulence-induced collision. The collision between drops is commonly considered similar to the collision between two gas molecules as in kinetic theory of gases.\(^{74}\) Collision frequency model with the assumption of binary collisions is given by Coulaloglou and Tavlarides (1977)\(^{48}\) with slight modification by Hsia and Tavlarides (1983)\(^{67}\) where the term \( \left( d_i^2 + d_j^2 \right) \) in original model is replaced by \( \left( d_i + d_j \right)^3 \). The modified model is

\[
h(d_i, d_j) = c_{1A} \frac{d_i^{1/3}}{(1 + \phi)} \left( d_i + d_j \right)^2 \left( d_i^{2/3} + d_j^{2/3} \right)^{1/2}
\]  
(87)

The model was adjusted by Tsouris and Tavlarides (1994)\(^{71}\) in the form of

\[
h(d_i, d_j) = \frac{\pi^{1/2}}{\sqrt{2}} \frac{d_i^{1/3}}{2} \left( d_i + d_j \right)^2 \left( d_i^{2/3} + d_j^{2/3} \right)^{1/2}
\]  
(88)

where it contains only one adjustable parameter, \( \alpha_n \) from the turbulent energy spectrum.

**Coalescence Efficiency Model.** Coalescence frequency models are developed based on different approaches to visualize the mechanism of coalescence process in the system. Three models have been developed for coalescence efficiency, which are energy, approach velocity and film drainage model.

Critical Approach Velocity: For critical approach velocity model which was derived for coalescence between bubbles by Lehr et al., (2002),\(^{75}\) the outcome of collision between two bubbles depends on the approach velocity of the colliding bubbles. The maximum velocity which caused coalescence is called critical velocity and the coalescence efficiency is written as

\[
\lambda(d_i, d_j) = \min \left( \frac{u_{\text{crit}}}{u_{\text{rel}}}, 1 \right)
\]  
(89)

This model is an empirical model where the critical velocity for coalescence is determined experimentally while energy and film drainage model is developed based on physical process of coalescence.

Energy Model: The energy model is proposed by Howarth (1964)\(^{76}\) where the probability of immediate coalescence increases with increase in the energy of collision. Thus, immediate coalescence occurs if the approaching velocity of two colliding drops exceeds a critical value. Based on this approach, models are developed in the form of

\[
\lambda(d_i, d_j) = \exp \left( -c_i E_i / E_{\text{kin}} \right)
\]  
(90)

where \( E_i \) is the interfacial energy and \( E_{\text{kin}} \) is the kinetic collision energy. Based on this approach, coalescence efficiency function that represents the immediate coalescence was proposed by Sovova (1981)\(^{77}\) and is given as

\[
\lambda(d_i, d_j) = \exp \left( \frac{C_{52} \sigma (d_i^2 + d_j^2) (d_i^{2/3} + d_j^{2/3})}{\rho_d g a^{2/3} d_i^{2/3} d_j^{2/3}} \right)
\]  
(91)

This approach does not consider the drainage and rupture of intervening film between drops which leads to development of film drainage model. In film drainage model, coalescence efficiency is determined from two characteristic time scales, which are contact time between colliding drops and drainage time. The latter is the thinning time of the intervening film to a critical thickness where the reduction in thickness is due to the force applied by turbulence.\(^{8} \) Therefore, coalescence only occurs if the contact time is longer than the drainage time. An expression for the model based on these timescales is given by Coulaloglou and Tavlarides (1977)\(^{48}\) as

\[
\lambda(d_i, d_j) = \exp \left( - \frac{t_{\text{drainage}}}{t_{\text{contact}}} \right)
\]  
(92)

The drainage time, \( t_{\text{drainage}} \) depends on the rigidity of drops surface and the mobility of contact interface while the contact time is determined by dimensional analysis or empirical expressions. The drainage time is derived based on the mobility of the colliding interface (i.e., immobile, partially mobile, or fully mobile) where the coalescence time for mobile interfaces is shorter than immobile interface.\(^{78}\) The mobility can be influenced by surface tension gradient or viscosity of the drops, where increase in both parameters lead to immobility of the interfaces, decreasing in coalescence efficiency.\(^{4} \)

The contact time for drops in turbulent dispersion is considered to be dependent on the size and turbulent velocity of the drops which is based on the energy dissipation rate.\(^{55}\) Therefore, the contact time in turbulent flow is estimated by

\[
t_{\text{contact}} = d^{2/3} / \nu^{1/3}
\]  
(93)

The coalescence efficiency model based on this approach was given by Coulaloglou and Tavlarides (1977)\(^{48}\) and are shown in Table 3. It shows that coalescence efficiency to the function of physical properties, drop diameter and energy input.

Various expressions of contact time have been reported in the literature. Contact time which is based on empirical expression such as the model used by Tsouris and Tavlarides (1994)\(^{71}\) is written as

\[
t_{\text{contact}} = \left( \frac{2.5ND^2}{L(T^2H)^{1/3}} \right)^{-1}
\]  
(94)

where \( H \) is the tank height, \( T \) is vessel diameter, \( D \) is impeller diameter, and \( L = 0.08D \). Examples of available coalescence efficiency model are also shown in Table 3.

**Values of model parameters**

For breakage and coalescence kernels that contain model parameters, the values assigned for the model parameters are...
important as they have strong influence on the simulation result. The constants which are functions of physical properties should be independent of the operating conditions and the values are determined by fitting of experimental data for a given system. Although it is suggested that the parameters should be universal in character in the case of similar hydrodynamic conditions, the use of original values suggested in original publications usually gives deviation between simulation and experimental data and thus, modified values were used (Table 4). The deviations may be caused by the limited physics represented by kernels and various assumptions which are not fully satisfied by actual processes such as the assumption of locally isotropic homogenous flow while high possibility of dispersion nonhomogeneity should be expected in real process.

There are still no specific values of model parameters agreed by researchers where various values have been proposed by even for a similar model. The optimized values obtained by recent researchers for models of Coulaloglou and Tavlarides are shown in Table 4. It is observed that different values have been obtained for the breakage and coalescence kernels. The different might be attributed by the different approaches in determining the parameters although most of the approaches have been based on trial and error attempts to reproduce experimental results. Ribeiro et al., (2011) developed an optimization tool which was tested on the determination of constants in the models of Coulaloglou and Tavlarides (1977). The work showed that the constants values obtained by the authors are in agreement with the older values reported in literature. The authors also showed that the assumption of negligible drop coalescence caused inaccurate result, resulting in high deviation between predicted and experimental DSD.

In the work by Azizi and Taweel (2011) model parameters were determined for liquid–liquid contacting system by screen-type static mixers, which was claimed to produce radially uniform turbulence conditions. The values of the parameters obtained by considering the spatial variation in the energy dissipation rates deviates in several orders of magnitude (See Table 4) compared to other parameters, which assumed uniform local energy dissipation rate through entire volume. Therefore, it is important to account for the variation in the energy dissipation rates and nonhomogeneity throughout the volume in estimating the model parameters so that the determined parameters can be used for various systems.

Therefore, the deviation between values of parameter may be caused of different solution techniques. In a recent work by Solsvik et al., (2014) a comprehensive statistical study of the fit to determine model parameters were performed and the author concluded that more successful parameter estimation can be achieved by assessing the problem formulation and the fit systematically.

Applications of various PBE models

The submodels used to simulate the dispersion process are chosen or derived based on the characteristics of systems being studied where the models should be able to represent the actual process. As various submodels are available in the literature, a number of recent studies have been conducted in which the results of simulation by different models are compared with experimental data. The models derived based on

### Table 3. Examples of Coalescence Efficiency Model for Different Interface Properties

<table>
<thead>
<tr>
<th>References</th>
<th>Coalescence Efficiency Model</th>
<th>Drops Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulaloglou and Tavlarides (1977)</td>
<td>$\lambda(d, d') = \exp \left( -C_k \frac{\mu_l \rho_c g}{\kappa} \left( \frac{d d'}{d + d'} \right)^k \right)$</td>
<td>Immobile</td>
</tr>
<tr>
<td>Alopaeus et al. (1999)</td>
<td>$\lambda(d, d') = \frac{0.26144}{k + 1}$</td>
<td>Partial Mobile</td>
</tr>
<tr>
<td>Liu and Li (1999)</td>
<td>$\lambda(d) = \frac{16.3 \left( \frac{d}{d_c} \right)^{2.3} \left( \frac{\rho_f}{\rho_l} \right)^{0.26}}{1 + \frac{d}{d_c}}$</td>
<td>Immobile Mobile</td>
</tr>
<tr>
<td>Prince and Blanch (1990)</td>
<td>$\lambda = \frac{\pi}{a} \sum_{i=1}^{n} n(i, 0) \tilde{S} \exp(\frac{5}{k})$</td>
<td>Deformable</td>
</tr>
</tbody>
</table>

### Table 4. Values of Parameters in Breakage Frequency and Coalescence Efficiency by Coulaloglou and Tavlarides (1977)

<table>
<thead>
<tr>
<th>References</th>
<th>System</th>
<th>$C_{1,h}$</th>
<th>$C_{2,h}$</th>
<th>$C_{1,v}$</th>
<th>$C_{2,v}$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulaloglou and Tavlarides</td>
<td>Stirred Vessel (Rushton Turbine)</td>
<td>0.00487</td>
<td>0.0552</td>
<td>0.000217</td>
<td>2.28 × 10$^{14}$</td>
</tr>
<tr>
<td>Schmidt et al. (2006)</td>
<td>Rotating Disc Contactor</td>
<td>–</td>
<td>–</td>
<td>0.036</td>
<td>1.152 × 10$^{10}$</td>
</tr>
<tr>
<td>Maaß et al. (2010)</td>
<td>Stirred Vessel (Retreat Curve Impeller)</td>
<td>0.003411</td>
<td>0.07588</td>
<td>0.2914</td>
<td>3.583 × 10$^{17}$</td>
</tr>
<tr>
<td>One-zone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maaß et al. (2012)</td>
<td>Screen Type Static Mixers</td>
<td>0.01397</td>
<td>0.3326</td>
<td>0.2914</td>
<td>3.583 × 10$^{17}$</td>
</tr>
<tr>
<td>Ribeiro et al. (2011)</td>
<td>Stirred Vessel (Rushton Turbine)</td>
<td>0.004664</td>
<td>0.03175</td>
<td>0.001</td>
<td>5.446 × 10$^{12}$</td>
</tr>
<tr>
<td>Maaß et al. (2012)</td>
<td>Stirred Vessel (Flat Blade Impeller)</td>
<td>0.022</td>
<td>0.33</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
the various mechanism discussed in this review have been applied successfully to simulate or reproduce experimental data by recent researchers with possible extension being proposed for wider range applications.

The PBE models in the form proposed by Coulaloglou and Tavlarides (1977)\(^4\) (Eq. 34 for breakage frequency, Eq. 87 for collision frequency and Eq. 95 for coalescence efficiency) were successfully applied by many researchers. Until recently, the models were used to simulate breakage and coalescence process such as in the works conducted by authors listed in Table 4. Alopaeus et al. (2002)\(^6\) have successfully applied the combination of breakage frequency model by Narsimhan and Gupta (1979)\(^5\) (Eq. 79), DSD model by Hsia and Tavlarides (1983)\(^\text{61}\) (Eq. 82) collision frequency by Coulaloglou and Tavlarides (1977)\(^4\) (Eq. 87) and a coalescence efficiency model by Tsouris and Tavlarides (1994)\(^\text{71}\) (Eq. 96) to simulate the DSD in stirred vessel using Rushton turbine as impeller.

To compare different breakage kernels, Maab et al. (2012)\(^4\) applied breakage kernels developed based on different mechanisms which are turbulent kinetic energy (Coulaloglou and Tavlarides (1977),\(^4\) Eq. 34 and its extended version, Eq. 37) and velocity fluctuations (Alopaeus et al., 2002)\(^6\) Eq. 79 and its extended version, Eq. 80) for breakage dominated system in a stirred tank. The simulation results by all models were in good agreement with the experimental data at low dispersed phase fraction and viscosity. Therefore, different breakage kernels could be used for a similar system provided that the model parameters in each model are fitted to a similar set of experimental data. However, at high dispersed phase fraction and viscosity, only prediction by improved or extended breakage kernel (Eq. 37) gives low deviation from experimental data which shows that the kernels are improved for wider ranges of application.

Instead of using a single breakage or coalescence kernels, different kernels could also be combined to determine the breakage and coalescence rate to describe the dispersion process such as in the work by Raikar et al., (2009)\(^\text{31}\) for emulsion in high-pressure homogenizer. The author modified the breakage kernel by Coulaloglou and Tavlarides (Eq. 34) for high pressure application using the relation between energy dissipation rate, \(\varepsilon\) and homogenization pressure, \(P\)

\[
\varepsilon = c_P P^{3/2} V^{-1/3} \rho_d^{-3/2}
\]

The resulting breakage kernel for breakage resulting by drop collision with turbulent eddies is given as

\[
g_1(V) = c_{1,b} V^{-1/3} P^{1/2} \rho_d^{-1/2} \exp \left[ -\sigma \left( \frac{1 + \phi}{\phi} \right)^2 \right]
\]

while breakage by shear turbulent shear is given as

\[
g_2(V) = c_{2,b} \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{p^{3/4}}{\mu_k \rho_d^{1/2} \rho_0^{0.5} V^{1/6}} \right) \exp \left[ -2c_{2,b} \sigma^2 \phi \left( \frac{p^{1/2} \rho_d^{0.5} V^{1/3}}{\mu_k} \right) \right]
\]

Assuming that both breakage mechanisms occurs simultaneously, a combined breakage kernel \(g(V)\) in the form of \(g(V) = g_1(V) + g_2(V)\) was applied. The combined kernel gives closer agreement to experimental data and is able to reproduce qualitative trends in the drop volume distribution at different system properties compared to when only one kernel (either \(g_1\) or \(g_2\)) is used.

**Nonhomogeneity in stirred vessel**

The breakage and coalescence process are mainly influenced by local turbulent dissipation in stirred vessel. The development of semiempirical correlations mostly assumed that the dispersion is well-mixed and uniformly distributed throughout the vessel which is acceptable for steady-state drop size measurement and for vessels short circulation time with low coalescence rate.\(^8\) To account for possible inhomogeneities in the vessel, the knowledge of local variations of flow and energy conditions is required as emphasized by Azizi and Taweel (2011)\(^\text{68}\) where it is best determined from experimental data. Advance tools such as CFD has also been used to determine the properties of flow field in the system and the comparison between model predictions by CFD and experimental data might also be of interest in some studies.

CFD have been applied by several authors to take into account the possible inhomogeneities in the system. Alopaeus et al.,\(^\text{26,62}\) conducted simulation using CFD to determine the flow data in which the stirred vessel in their work was divided into 11 subregions. This is to consider for the variation in turbulent energy dissipation at different area in the vessel in which the energy dissipation near the impeller region is several orders of magnitude greater than away from it. The multiblock model approach is more realistic and could be used to give better parameter values compared to single block model. Similar approach was taken by Srilatha et al., (2010)\(^\text{55}\) by dividing the vessel into up to eight zones to take into account the variation of drop sizes with spatial location. Maab et al., (2010)\(^\text{35}\) also have shown that PBE with two-zone model gives very satisfying prediction compared to one-zone model. The different between the zonal-model can be seen from the value of parameters, where values obtained by two-zone model are an order of magnitude higher than the one-zone model (see Table 4). The two-zone model is successfully applied to simulate the process and capable of displaying the effects of various parameters such as impeller speed, impeller height liquid level and baffle length on drop sizes with deviations less than 10% between predicted and calculated \(d_32\). The author also proposed that the PBE-zonal-model can further be improved to describe transient drop size if a detailed knowledge on flow field is available, which can be achieved by CFD. It has reached a level of reliable and accurate result for the prediction of flow field and hydrodynamics in stirred vessel which is highly related to drop size evolution.\(^\text{83}\)

Coupling CFD with PBE model has also been done by Håkansson et al., (2009)\(^\text{68}\) for a high pressure homogenizer where large velocity gradient in comparison to the very small geometrical scales are involved. Therefore, the drop breakage and coalescence process varies across the spatial location in the homogenizer. In a separate work by Håkansson et al., (2009),\(^\text{85}\) a dynamic simulation model was developed for emulsion formation in a high pressure homogenizer. Based on the developed model, a representative description of emulsification process in a high pressure homogenizer is obtained as a function of flow coordinate. Therefore, it could be used to study spatial fragmentation (breakage) and recoalescence in active region of homogenization. In the work, the flow field in the active region is calculated by CFD in which the flow field is then used to discuss and verify the results of simulation obtained by the dynamic simulation.

**Conclusions**

Earlier correlations and models in which the applications are limited to inviscid and low dispersed phase have been
modified after considering various parameters such as viscosity and dispersed phase fraction on mean drop size. Semiempirical correlations developed by experimental data are simple and easy to be used compared to PBE. They are able to reproduce experimental data with low deviations. However, the correlations are limited to steady state or stationary drop size predictions which mostly assume homogenous dispersion in the vessel. Therefore the correlations only consider the averages for the whole vessel and are highly system specific.

Various PBE submodels have been developed from different drop breakage processes but they are based on the same mechanism which is turbulent pressure fluctuations. Suitable models should be chosen based on the mechanism and properties of the system being studied. For models with adjustable parameters, different classes of models can be used for a same system if the parameters are properly estimated by fitting of experimental data. However, to determine the parameters which could be used in various system and operating conditions is still a challenge.

With the use of PBE, transient drop size can be estimated and the possible inhomogeneity in stirred vessel can be accounted by including the spatial variation in the vessel. The accuracy of the models can be improved with a detailed knowledge of the flow field in the vessel which can be obtained by the use of advanced tools such as CFD. By pairing PBE-zonal-model with a detailed knowledge on flow field which can be obtained by CFD, a highly reliable tool to describe the transient drop sizes in stirred liquid–liquid dispersion can be produced.

Acknowledgments

The authors are grateful to the University of Malaya High Impact Research Grant (HIR-MOHE-D00038-16001) from the Ministry of Higher Education Malaysia which financially supported this work.

Notation

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>Gamma function</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>energy dissipation rate, $m^2/s^3$</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>continuous phase density, $kg/m^3$</td>
</tr>
<tr>
<td>$\mu_c$</td>
<td>continuous phase viscosity, $kg/ms$</td>
</tr>
<tr>
<td>$\mu_d$</td>
<td>dispersed phase viscosity, $kg/ms$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>interfacial tension, $N/m$</td>
</tr>
<tr>
<td>$n_0$</td>
<td>adjustable parameter for Eq. 49</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>collision efficiency</td>
</tr>
<tr>
<td>$\beta$</td>
<td>drop size distribution</td>
</tr>
<tr>
<td>$\xi$</td>
<td>ratio of eddy to drop size</td>
</tr>
<tr>
<td>$\phi$</td>
<td>dispersed phase fraction</td>
</tr>
<tr>
<td>$\phi_d$</td>
<td>dispersed phase density, $kg/m^3$</td>
</tr>
</tbody>
</table>

Letters and subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>normalization factor of beta function</td>
</tr>
<tr>
<td>$B_0$</td>
<td>birth by coalescence</td>
</tr>
<tr>
<td>$D_{ac}$</td>
<td>capillary number, dimensionless</td>
</tr>
<tr>
<td>$D$</td>
<td>impeller diameter, $m$</td>
</tr>
<tr>
<td>$D_k$</td>
<td>death by breakage</td>
</tr>
<tr>
<td>$D_d$</td>
<td>death by coalescence</td>
</tr>
<tr>
<td>$d$</td>
<td>drop diameter, $m$</td>
</tr>
<tr>
<td>$d_j$</td>
<td>daughter drop diameter, $m$</td>
</tr>
<tr>
<td>$d_i$</td>
<td>drop of diameter $i$, $m$</td>
</tr>
<tr>
<td>$d_{in}$</td>
<td>initial drop diameter, $m$</td>
</tr>
<tr>
<td>$d_p$</td>
<td>parent drop diameter, $m$</td>
</tr>
<tr>
<td>$d_{p, crit}$</td>
<td>critical elongated drop diameter, $m$</td>
</tr>
<tr>
<td>$d_{max}$</td>
<td>maximum drop diameter, $m$</td>
</tr>
<tr>
<td>$d_{S}$</td>
<td>Sauter mean diameter, $m$</td>
</tr>
<tr>
<td>$d_{S, d}$</td>
<td>Sauter mean diameter (dilute), $m$</td>
</tr>
<tr>
<td>$E_{kin}$</td>
<td>kinetic energy, $kgm^2/s^2$</td>
</tr>
<tr>
<td>$f_{hs}$</td>
<td>volume fraction</td>
</tr>
<tr>
<td>$g$</td>
<td>breakage frequency</td>
</tr>
<tr>
<td>$h$</td>
<td>collision frequency</td>
</tr>
<tr>
<td>$k$</td>
<td>wave number of eddy, $1/m$</td>
</tr>
<tr>
<td>$n_d$</td>
<td>number of drops per unit volume ($1/m^3$)</td>
</tr>
<tr>
<td>$t_{be}$</td>
<td>breakage elongation time, $s$</td>
</tr>
<tr>
<td>$t_{res}$</td>
<td>resident time, $s$</td>
</tr>
<tr>
<td>$t_{tb}$</td>
<td>turbulent breakage time, $s$</td>
</tr>
<tr>
<td>$S_0$</td>
<td>cross-sectional area for collision, $m^2$</td>
</tr>
<tr>
<td>$u$</td>
<td>velocity, $m/s$</td>
</tr>
<tr>
<td>$u_c$</td>
<td>critical velocity, $m/s$</td>
</tr>
<tr>
<td>$u_{res}$</td>
<td>turbulent velocity of eddies, $m/s$</td>
</tr>
<tr>
<td>$y$</td>
<td>mean number of daughter drops</td>
</tr>
<tr>
<td>$V$</td>
<td>volume of drop</td>
</tr>
<tr>
<td>$V_1$</td>
<td>viscosity number, dimensionless</td>
</tr>
<tr>
<td>$We$</td>
<td>Weber number, dimensionless</td>
</tr>
</tbody>
</table>

Abbreviations

- PBE = population balance equation
- DSD = drop size distribution
- CFD = computational fluid dynamics

Literature Cited


*Manuscript received June 26, 2014, and revision received Jan. 19, 2015.*