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Prediction of emulsion drop size distributions in colloid mills

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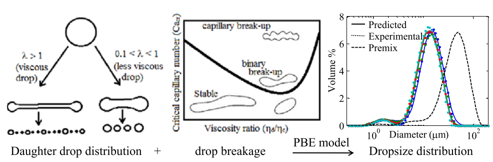
HIGHLIGHTS

- Developed a population balance equation model for emulsification in colloid mill.
- Derived the function for drop breakage frequency in simple shear flow.
- Proposed a new daughter drop distribution function for capillary drop breakage.
- Used a viscosity model to predict the emulsion viscosity at high shear rates.
- Demonstrated good agreement between measured and predicted drop size distributions.

GRAPHICAL ABSTRACT



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ABSTRACT

Colloid mills are the most common emulsification devices used in industry for products with high oil content. Drop breakage occurs when the emulsion is flowed through a small gap between rotor and stator under laminar shear conditions. In this paper, we have developed the first full population balance equation (PBE) model for colloid mills and used the model to better understand the relevant drop breakage mechanisms. The PBE model accounted for both drop breakage and coalescence and generated predictions of the drop size distribution after each pass of the emulsion through the colloid mill. Drops were assumed to break due to capillary instability with the distribution of drop sizes resulting from each breakage event studied in detail. A viscosity model was developed to predict the emulsion viscosity as function of the oil fraction and the high shear rates commonly used. Nonlinear optimization was used to estimate adjustable parameters in the breakage and coalescence functions to minimize the least-squares difference between predicted and measured drop size distributions for high oil-to-surfactant emulsions. We concluded that experimentally observed drop volume distributions could not be predicted with daughter drop distribution functions reported in the literature. Improved predictions were obtained using a new bimodal distribution function which captured drop breakage into multiple, nearly uniform daughter drops with a large number of small satellite drops. We also investigated model extensibility for changes in the oil fraction, emulsion flow rate and rotor speed.

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1. Introduction

Emulsions are heterogeneous system of two immiscible liquids in which one phase is dispersed in the other phase. Oil-in-water emulsions are commonly encountered in the food, pharmaceutical,

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agricultural, and consumer product industries. A minimal emulsion consists of water as the continuous phase, an oil as the dispersed phase and a surfactant that stabilizes formed oil droplets. The ingredients are mixed and drop sizes are reduced by applying mechanical energy to the emulsion. The size distribution of dispersed oil drops is a critical property of the emulsion that affects rheology, stability, texture, and appearance of the final product (McClements, 2005). The drop size distribution is known to depend on both the emulsion composition and the processing conditions (Walstra, 1993).

Emulsions are usually prepared via a two step process. In the first step, a coarse emulsion or premix is prepared by thoroughly mixing the ingredients in a low shear device. The coarse emulsion is then passed through a high energy mechanical device such as a high pressure homogenizer or a colloid mill. High pressure homogenization is generally preferred for low viscosity emulsions (Pandolfe, 1996) because sub-micron drops can be readily generated due to the high energy input. Colloid mills are the preferred technology for highly viscous emulsions (> 5000 cp) commonly encountered in industry. A typical colloid mill consists of a conical rotor that rotates inside a static stator. As the emulsion is passed through the narrow gap between the rotor and stator, drop breakage occurs due to intense shearing. Additional passes of the emulsion through the colloid mill allow the drop size to be further reduced. While drop breakage in simple shear or Couette flow has been well studied (Cristini et al., 2003; Zhao, 2007; Renardy et al., 2002; Grace, 1982; Boonen et al., 2010), drop breakage mechanisms in colloid mills are not well understood. Common practice is to assume simple or extensional shear flow, in which drops break due to capillary instability when the ratio of the viscous stress to the interfacial tension force crosses a critical value (Wieringa et al., 1996; King and Keswani, 1994; Almeida-Rivera and Bongers, 2012).

A mathematical model that generates pass-by-pass predictions of the drop size distribution for different formulations and processing conditions would be a very valuable tool for colloid mill design and operation. Population balance equation (PBE) models have been successfully used to predict size distributions for other particulate processing devices including liquid–liquid dispersers (Alopaeus et al., 1999, 2002, 2003; Coulaloglou and Tavlarides, 1977; Kostoglou and Karabelas, 2001; Sovova, 1981; Sovova and Prochazka, 1981), liquid–liquid extractors (Ruiz et al., 2002; Ruiz and Padilla, 2004; Simon et al., 2003), and high pressure homogenizers (Hakansson et al., 2009a,b). We have developed a series of increasingly sophisticated PBE models for high pressure homogenizers that account for both breakage and coalescence (Raikar et al., 2009, 2010; Maindarkar et al., 2012, 2012). Perhaps due to the focus on homogenization, very few PBE models have been presented for colloid mills despite their industrial significance. Wieringa et al. (1996) developed a simple PBE model based on the assumption that the drop breakage frequency was the reciprocal of the breakage time, which in turn depended linearly on the drop size. An empirical equation for the number of daughter drops formed as a function of the capillary number was derived. Coalescence was completely neglected under the assumption that sufficient surfactant was available in solution for stabilization of newly formed drops. Also under the assumption of negligible coalescence, Almeida-Rivera and Bongers (2010) modeled the frequency of binary drop breakage to be proportional to $(d_i - d_{max})^n$, where d_i is the drop diameter, d_{max} is the critical drop size below which drops cannot break, and n is an adjustable model parameter. In addition to providing few insights into the relevant drop breakage mechanisms, these PBE models are not capable of accurate prediction due to their restrictive assumptions.

In this paper, the first PBE model of a colloid mill is developed that includes both drop breakage and coalescence. Drop breakage was assumed to follow the usual capillary instability mechanism with the number of daughter drops formed by a breakage event studied in detail. A new daughter drop distribution function consistent with previous experimental studies was formulated to improve PBE model predictions. The drop breakage and coalescence functions depend on the emulsion viscosity. The PBE model was integrated with a viscosity model that allowed the emulsion viscosity to be predicted as a function of the oil content and extrapolated to high shear rates. Adjustable model parameters were determined by nonlinear least-squares estimation using drop size distributions measured for multiple emulsification passes. The model was used to evaluate model extensibility with respect to the oil fraction, emulsion flow rate and rotor speed.

2. Drop breakage and coalescence in colloid mills

When an emulsion is passed through the narrow gap between the stator and the rotor rotating at high angular velocity (Fig. 1(a)), drop tends to stretch due to the very high shear rate $\dot{\gamma}$ (10^4–10^6 1/s). When the ratio of the viscous stress acting on the drop to the interfacial tension force surpasses some critical value, a mother drop breaks into two or more daughter drops. This ratio is called the capillary number Ca and is defined as Janssen et al. (1994)

$$Ca = \eta_c \dot{\gamma} d / 2\sigma \tag{1}$$

where η_c is continuous phase viscosity; d is the mother drop diameter; and σ is the interfacial tension. The critical value is called the critical capillary number Ca_{cr} and depends on type of flow and the viscosity ratio of the dispersed and continuous phases ($\lambda = \eta_d/\eta_c$). The situation is more complicated in high oil emulsions because droplets interact with each other. In this case, the continuous phase viscosity η_c in the capillary number must be replaced by the apparent emulsion viscosity η_{em} and the viscosity ratio must be modified accordingly ($\lambda = \eta_d/\eta_{em}$).

Drop breakage in laminar shear flow is known to be very complex. When the capillary number is just slightly larger than the critical value such that $1 \le Ca/Ca_{cr} \le 2$, a drop breaks into two nearly equally sized daughter drops by an end-pinching mechanism (Region A in Fig. 1(b)) (Janssen et al., 1994; Wieringa et al., 1996; Zhao, 2007). When $Ca/Ca_{cr} >> 1$ and $0.1 < \lambda < 1$, a drop breaks into many nearly equally sized daughter drops by a capillary mechanism (Region C in Fig. 1(b), (c)). When $Ca/Ca_{cr} >> 1$ and $\lambda > 1$, a drop breaks into many unequally sized daughter or satellite drops (Region B in Fig. 1(b), (c)) (Zhao, 2007; Cristini et al., 2003). Adding to the complexity, Ca_{cr} is known to depend on the type of flow field in addition to the viscosity ratio. For example, drops with $\lambda > 4$ will almost never break in simple shear flow because Ca_{cr} is too large, but such drop can break in extensional shear flow as Ca_{cr} is much smaller (Fig. 1(d)). Furthermore, Taylor vortices can appear in the flow field when the Taylor number (Ta) exceeds some critical value (Ta_{cr}), which depends on the Reynolds number of flow. Taylor vortices have been experimentally observed for Reynolds number above 800 (Li et al., 2010). Simple calculations show that our emulsions prepared at 10 and 30 wt% oil will break due to Taylor vortices (Almeida-Rivera and Bongers, 2010) and not due to shearing in simple shear flow (Fig. 1(b)). The implications of this behavior for PBE modeling are discussed below.

Although colloid mills are designed to promote drop breakage, colliding drops may coalesce under certain conditions. The coalescence rate is determined by the frequency of collisions and the probability that a collision event will produce coalescence. The collision frequency depends on the local flow field, which is characterized by the local shear rate under laminar shear flow (Klink et al., 2011). By contrast, the coalescence probability depends on the ratio of the contact time between drops and the time required for drainage of the liquid film between the drops. The film