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Analysis of concentration polydispersity in mixed liquid–liquid systems

Ville Alopaeus*

Aalto University, School of Chemical Technology, Department of Biotechnology and Chemical Technology,
Chemical Engineering Research Group, Kemistintie 1, 02150 Espoo, Finland

ABSTRACT

Inter-phase mass transfer for each chemical component is typically modelled with one material balance for the continuous and one for the dispersed phase. This approach contains inherently an assumption that the phases are well mixed at least locally. For the dispersed phase, this assumption requires that breakage and coalescence are significantly faster compared to the mass transfer, which is not necessarily true. It is important to carry out preliminary assessment whether the dispersed phase segregation is important and should be considered in subsequent modelling efforts, before embarking heavy multidimensional simulations where all possible dispersed phase variations are considered. In this work, relevant time scales are first defined and used for analyzing dispersed phase mixedness in liquid–liquid systems with mass transfer between the phases. Then appropriate dispersed phase modelling tools for the purpose are evaluated. Simple droplet number density based analysis is shown to estimate mixedness reasonably well. Furthermore, the drop number density approach is also shown to predict the average drop sizes with almost comparable accuracy than the full population balances.

Keywords: Liquid–liquid dispersion; Population balances; Mass transfer; Mixing; Drop size; Polydispersity

1. Introduction

Adequate mixing in multiphase systems is very important in many fields of chemical process industries. There are several reasons for this, such as effective mixing of reagents that are only partly miscible, perform reactions where distribution between the phases is utilised to improve conversion, e.g. by removing equilibrium reaction products from the reacting phase, or provide sufficient mass transfer area in separation processes, such as in extraction. Besides adequate mixing in practice, it is important to be able to model these processes accurately so that new mixing processes can be developed and designed in an optimal way.

Modelling of most chemical engineering processes involves formulation of material balances for at least two phases, and modelling of mass transfer between these phases. This methodology encompasses basically the whole field of separation processes design, where separation of two or more chemical components is based on differences in their distribution between the phases. It is also of fundamental importance in most multiphase reactors, especially when two fluid phases are present.

In these modelling efforts, typically several simplifying assumptions are made in order to ease the computational burden. Sometimes these assumptions are clearly oversimplifications of the physical reality. In these cases it is important to assess how big errors may result in from such simplifications.

Perhaps the most typical simplifying assumptions are related to the flow pattern. In most cases of intensively flowing or mixed multiphase fluid flows there are regions of high turbulent intensity, but also more quiescent regions. However, traditionally stirred tanks or stages of an extractor have been assumed ideally mixed. The local variations in flow conditions, however, affect the bubble and drop population dynamics, and hence the operation of the vessels (Alopaeus et al., 2008). This can be accounted in a rather straightforward, although in many cases computationally demanding, manner, by simultaneously modelling fluid flow, multiphase behaviour, and chemical reactions (Dudukovic et al., 1999; Jakobsen et al., 2005; Moilanen et al., 2006, 2008; Ranganathan

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* Tel.: +358 400 740 807.
E-mail address: Ville.Alopaeus@aalto.fi

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Nomenclature

A	agglomeration (coalescence product distribution) table
B	breakage table
D	diffusion coefficient in the dispersed phase (m^2/s)
F	coalescence rate (m^3/s)
Fo	Fourier number for mass transfer
g	breakage rate (1/s)
k	mass transfer coefficient (m/s)
L	length (m)
n	number density of droplets
N_{DMM}	dispersed phase mixedness with respect to mass transfer
p	physical property vector
S	sensitivity
t	time (s)
Y	particle number concentration ($1/m^3$)
β	daughter drop size distribution
δ	differential change
ε	turbulent energy dissipation rate (m^2/s^3)
ϕ	dispersed phase volume fraction
ρ_c	continuous phase density (kg/m^3)
ρ_d	dispersed phase density (kg/m^3)
σ	interfacial tension (N/m)
τ_L	characteristic life time (s)
τ_M	characteristic time for mass transfer (s)

and Sivaraman, 2011; Buffo et al., 2012). Another modelling detail that needs further analysis is mass transfer rate. The most rigorous and physically justifiable approach is to divide mass transfer rate into two parts: mass transfer flux and mass transfer area, where the mass transfer area is best described by using population balances. The mass transfer fluxes are typically calculated by using mass transfer coefficient correlations and driving forces estimated based on material balances, although more detailed flow and concentration field calculations have also been reported (Piarah et al., 2001; Kröger et al., 2007).

There are, however, some further details or assumptions that are scrutinised or even mentioned in only a few papers (Curl, 1963; Guimares and Cruz-Pinto, 1988; Guimares et al., 1990). These are:

(1) Mass transfer coefficient is typically estimated by using the average bubble or droplet size, and hence only a size-averaged value for the mass transfer flux is used.
(2) Dispersed phase volume fraction is often calculated by using an average settling velocity for different bubble and drop sizes. This is justified only in such cases where settling velocities for different bubble or droplet sizes are of the same order of magnitude.
(3) Dispersed phase is assumed to be completely mixed, i.e. all bubbles or droplets are assumed to share the same concentration field, at least locally. If bubble and droplet breakage and coalescence are fast phenomena compared to equilibration of the chemical components, this is expected to be a valid assumption due to averaging of the concentrations in breakage and coalescence processes; otherwise the assumption is questionable. In order to address this thoroughly, at least two-dimensional population balances would be needed to describe the mass transfer process. One dimension describing dispersed phase state should be related to bubble or droplet size (diameter or volume), and other related to their composition (concentration or mass of a component). Dispersed phase mixing (although without mass transfer) was recently proposed as a test case for two-dimensional population balance models (Chauan et al., 2010). The problem of polydispersity in aerated stirred tanks is also recently studied by Buffo et al. (2012, 2013) with computational fluid dynamics combined with multidimensional population balances. It is clear that those simulations are computationally expensive, and a preliminary assessment to reveal the need for such efforts is welcome.

In this contribution, the first and third of these assumptions are discussed in more detail with a sensitivity analysis related to the effects of dispersed phase volume fraction, turbulent energy dissipation and physical properties. This is done by comparing relevant time scales for mass transfer and droplet breakage and coalescence. Although time scale analysis has been very fruitful in many chemical engineering related problems, such as in analysis of turbulent mixing where turbulence time scales are compared to reaction time scales (Brodkey, 1975), and rate limiting steps in chemical reactions where diffusion and intrinsic reaction rate time scales are relevant (Froment and Bischoff, 1990), it has not been applied to the present mixing problem. In addition to the time scale analysis, a new method is proposed for simultaneous estimation of mean drop diameter and a dimensionless number describing dispersed phase mixedness, without rigorous solution of discretised population balances. This is an important practical tool since it can be used to analyze the need for further, potentially very resource demanding, modelling efforts with multidimensional population balances where actual concentration variances within the droplet phases need to be resolved. This preliminary analysis for dispersed phase mixedness could be carried out as systematically as the Reynolds number is currently calculated in order to predict the flow regime and the need for further turbulence modelling. Despite its simplicity and an obvious need for it, the present time scale analysis related to the dispersed phase mixedness is not reported in the literature.

2. Time scales of mass transfer and droplet renewal

Mass transfer into or out from bubbles or droplets is inherently time dependent, since these fluid elements enclose closed volumes as long as the elements retain their identity. In the mass transfer analysis, it is typically assumed that droplets are initially at uniform compositions, and approaches equilibrium during contact with the continuous phase. At short contact times, mass transfer is relatively fast due to large concentration gradients near the droplet surface, but slows down at longer contact times.

Time dependent mass transfer is analysed here by assuming that the controlling resistance is inside the droplets, so that the surface concentration remains essentially constant during the droplet life time. This is approximately the case for transfer of such components which preferably concentrate in the continuous phase. Mass transfer rate in such systems