On the Applicability of the Grace Curve in Practical Mixing Operations


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Abstract

Although the ‘Grace curve’ is often used to select the material components and optimal flow rates in blending operations, its validity for industrial mixing practice remains to be seen. Apart from the fact that the final dispersion is finer than predicted by the curve once the imposed capillary number is much larger than the critical one, the flow field in industrial mixers is not homogeneous. This causes the actual shear/elongation rate imposed upon a (moving) droplet to be time-dependent. To investigate the importance thereof, analytical models are used which describe the droplet stretching rate as a function of the droplet shape, viscosity ratio and time-varying capillary number. Both experiments and model predictions show that droplet breakup can be caused by inhomogeneous flow fields, even if the average capillary number is sub-critical. Moreover, the model predicts how the critical capillary number is influenced by a non-spherical initial shape. At higher aspect ratios the critical capillary number can be reduced significantly, especially for higher viscosity ratio droplets.

Keywords: Grace curve, blends, analytical model, droplet elongation rate

Introduction

The existence of the large number of different types of commercial mixers indicates the relevance of the dispersion of immiscible liquid/liquid systems for industrial practice. Depending on the mixer design and its operating conditions, a final morphology results from the mixing process. Since this morphology has a large influence on the final properties of the product, dispersive mixing has received considerable attention in the literature in the last century. One of the essential steps in the mixing process is the deformation and breakup of a single dispersed droplet in a second immiscible liquid, see e.g. Taylor (1932, 1934). Apart from the reviews given by Rallison (1984), Stone (1994), Acrivos (1983) and Sadhal et al. (1997), the paper which is probably most refereed is the work of Dr Harold P. Grace presented at the 3rd Engineering Foundation Conference on Mixing in 1971, which was republished in Chemical Engineering Communications (Grace, 1982). The most used graph in the field of dispersive mixing is probably the ‘Grace-curve’. Although the Grace curve is based on a multitude of sound experiments, and later predicted by elegant modeling, it has severe limitations when applied to industrially relevant mixing processes. One limitation was already clarified by Janssen & Meijer (1993) and was based on the fact that in industrial mixing processes the capillary number is generally much larger than the critical capillary number. The second limitation, which is the topic of this paper, is due to the fact that in all practical mixers the flow field is inhomogeneous.

Grace Curve

To obtain the Grace curve, numerous experiments on the deformation and breakup of single drops were performed in both shear and elongational flow. In these experiments, an initially spherical Newtonian
A droplet is inserted in a Newtonian continuous phase. The flow rate of the continuous fluid is very slowly increased from zero until binary breakup is observed.

The ratio between the dispersed phase viscosity \( \eta_d \) and the continuous phase viscosity \( \eta_c \), referred to as the viscosity ratio \( \lambda \), was varied over seven decades, while the range of the continuous phase viscosity was changed over a range of two decades. To collapse all these experimental results into a single curve, the capillary number, first introduced by Taylor (1934), was used. This capillary number \( Ca \) is the ratio of the viscous forces \( \eta_c \dot{\epsilon}_c \) to the interfacial forces \( \sigma / R \), where \( \dot{\epsilon}_c \) denotes the flow rate of the continuous phase, \( \sigma \) is the interfacial tension and \( R \) is the equivalent droplet radius.

The Grace curve, see figure 1, shows the relation between the viscosity ratio \( \lambda \) and the critical capillary number \( Ca_c \), at which a single, initially spherical droplet bursts in a homogeneous, quasi steady flow. Above this critical capillary number, the droplet can no longer assume a steady shape and, in time, it will breakup.

Based on the required droplet size of the blend, the Grace curve can be used to determine the necessary shear/elongation rate for binary breakup of a single initially spherical Newtonian droplet in a quasi-steady homogeneous Newtonian flow. Although these conditions are easily satisfied in laboratory experiments, they are usually not present in industrial mixing devices.

### Binary vs. Capillary Breakup

Unless the flow rate is increased slowly, giving the droplet the time to breakup as soon as its critical capillary number is reached, e.g. in a repeated process of binary breakup, the droplet will be extended into a liquid thread that will be distorted by capillary breakup. As the flow suppresses the Rayleigh distortions, the thread may thin considerably before breakup occurs, resulting in finer dispersions than those predicted by the Grace curve, see Tomotika (1936), Mikami et al. (1975), Khakhar & Ottino (1986). As was shown by Tjahjadi & Ottino (1991), and by Janssen & Meijer (1993, 1995) the completely different deformation and breakup process results also in a different optimum viscosity ratio. In contrast to the prediction of the Grace curve (\( \lambda_{opt} = 1 \)), even in shear dominated flow the finest dispersions are found at the higher viscosity ratios.

### Inhomogeneous Flow

Besides, the flow field in industrial mixers is, in general, not homogeneous. The flow rate experienced by a moving droplet will therefore be time-dependent. This time dependence has an influence on the mixing process, as is shown in figure 2. The figure shows two single drop experiments in a hyperbolic flow. In both experiments the capillary number is first increased from zero to \( 1.2Ca_c \) and then decreased again to zero. In the first experiment, the maximum capillary number is reached 50 seconds after the start of the experiment: the droplet deforms as the capillary number is increased and then retracts back to a sphere again. In the second experiment, the rate at which the capillary number is increased is lower and the maximum capillary number is reached in 56 seconds. In this case, the droplet does not retract back to a sphere. Instead the droplet continues to elongate until breakup occurs. Note that in both experiments the average capillary number is below the critical capillary number. Therefore, a more general drop deformation model is needed.

### Modeling of Shape-Dependent Droplet Deformation Rate

Although the actual breakup time and final droplet size distribution depend on the breakup mode, one can determine whether breakup will occur based on the deformation solely. The breakup criterion then has to be redefined as follows: A droplet will break up if its length is larger than the critical length for a sufficient amount of time. The critical length is defined as the droplet length above which the droplet can not assume a steady droplet shape under steady flow conditions.

To describe the droplet deformation in a time-dependent experiment such as shown in figure 2, the model should predict a droplet deformation rate which is not only a function of the capillary number, but also of the instantaneous droplet length. Such models have been described by Buckmaster (1973), Hinch & Acrivos (1980), Khakhar & Ottino (1986), Stegeman et al. (1999) and Jackson & Tucker (2001). All five models give an expression for the deformation of a single, neutrally buoyant, Newtonian droplet immersed in a viscous Stokes flow as a function of the material parameters, the instantaneous flow rate and
the instantaneous dimensionless droplet length $L$. The first three models assume a slender droplet of low viscosity ratio. For an axisymmetrical elongational flow, they reduce to:

$$\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} = 1 - \frac{\sqrt{L}}{2\sqrt{5} Ca (1 + 0.8\lambda L^3)}$$  \hspace{1cm} (1)$$

where $\dot{\epsilon}_d$ and $\dot{\epsilon}_c$ are the elongation rates of the droplet and the continuous phase respectively. In the model of Buckmaster (1973), the constants $2\sqrt{5}$ and 0.8 are replaced by 4 and 1, respectively. The fourth model also assumes a slender droplet, but does not make any assumptions about its viscosity ratio. It is only derived for axisymmetrical elongational flows (Stegeman et al., 1999) and yields:

$$\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} = \frac{\dot{L}}{\epsilon_c L} = \frac{1 + L^{-3} \left( \frac{2}{3\lambda} + \frac{5}{12} - \frac{g}{fCa} - \frac{g}{4\lambda Ca} \right)}{1 + L^{-3} \left( \frac{3}{4} + \frac{1}{2\lambda} + \frac{4\lambda}{3f} - \frac{2}{3f} \right)}$$  \hspace{1cm} (2)$$

where $f$ and $g$ only depend on $L$:

$$f = \frac{1}{\ln(2\sqrt{L^3})} + \frac{1.5}{[\ln(2\sqrt{L^3})]^2} \hspace{1cm} g = \frac{\sqrt{L} (L^6 + 2L^3 - 3)}{2L^6}$$  \hspace{1cm} (3)$$

where again $L$ is the droplet length divided by the radius of an equivalent spherical droplet. The implicit model by Jackson & Tucker (2001) is based on the deformation model of Wetzel & Tucker (2001). No assumptions on slenderness or viscosity ratio are made. This model states:

$$\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} = F(\lambda, Ca, D, W, C, B)$$  \hspace{1cm} (4)$$

where $D$ and $W$ are the rate of deformation and vorticity tensor respectively. The fourth order tensors $C$ and $B$ are functions of the viscosity ratio and the fourth order Eshelby and alternate Eshelby tensor, which in turn depend on the droplet shape.

MODEL SELECTION

To select the best model for this study, the model predictions are compared in figure 3. For the first four models, the Grace curve and the droplet deformation rate can be directly computed from equations (1) through (3). The numerical results for the last model was obtained by using a code kindly provided by Jackson and Tucker.

Since this study is on the Grace curve, the model predictions of the critical capillary number as a function of the viscosity ratio are determined, and compared to experimental results. As is shown in figure 3, the first type of models give an excellent agreement with the experimental results for low viscosity ratio’s. Due to the low viscosity ratio assumption, the poor performance for high viscosity ratio droplets could be expected. The model by Stegeman et al. (1999) predicts the Grace curve reasonably well for all viscosity ratio’s, whereas the model by Jackson & Tucker (2001) performs nicely for high viscosity ratio droplets, but greatly underestimates the critical capillary number for low viscosity ratio droplets.

Since equation (1) was derived for low viscosity ratio droplets, the models are also compared on their prediction of the droplet deformation rate of a droplet with viscosity ratio 0.01. As is shown in figure 3, the last two models qualitatively predict the same behavior. Equation (1) however, predicts a negative droplet elongation rate for $L = 1$ at sub-critical capillary numbers. Physically, this is incorrect, since $L = 1$ corresponds to a spherical droplet. A negative droplet elongation rate would therefore imply droplet elongation in a direction perpendicular to the flow. Therefore, equation (2) will be used in the remainder of this paper.

GRAPHICAL REPRESENTATION

Figure 4 gives a graphical representation of equation 2 for $\lambda = 1$. Although the arrows appear to form a continuous curve, the graph should not be read as such. In general, the graph is to be read as an collection of points which show the relation between the length and the relative elongation rate of the droplet for any instantaneous capillary number. Only in the case of a constant capillary number, the graph can be read along the ‘lines’, following the direction of the arrows.
STEADY ELONGATION RATE
Suppose that we insert an initially spherical droplet \( (L = 1) \) in a continuous phase with a constant elongation rate \( \dot{\epsilon}_c \) corresponding with half the critical capillary number. Figure 4 predicts that in this case the initial relative droplet elongation rate is 0.87. As the droplet becomes larger, the relative droplet elongation rate decreases. The droplet will therefore deform ever slower, until it reaches its steady state. At that moment the length of the droplet is 1.37 times its initial radius. The assumed droplet shape is stable against small perturbations, since a slightly longer droplet at this capillary number will decrease in length, while a slightly shorter droplet will increase in length.

The critical capillary number can now be defined as the highest capillary number where a steady droplet shape can just be found. This shape, however, is no longer stable against small perturbations. Although a slightly shorter droplet will still increase in length, a slightly larger droplet will no longer decrease in length. Instead it will elongate ever faster and will finally breakup. At supercritical capillary numbers no steady droplet shape can be found at all and all droplets will eventually break up.

TIME DEPENDENT FLOW
In the more complicated case where the capillary number is not constant, the graph should be read as a collection of points. The evolution in time of the droplet length can be calculated with the integral:

\[
L(t) = \int_{-\infty}^{t} \frac{CaL + L^{-2}}{1 + L^{-3}} \left( \frac{2}{3} \frac{Ca}{12} - \frac{g}{7} - \frac{9}{3} \right) \frac{\sigma}{\eta_c \bar{R}} \, \text{d}t
\]

Figure 5 shows an example of the evaluation of the droplet length for a specific elongation rate as a function of time: An initially spherical droplet (5b) is subjected to an elongational flow with \( Ca = 0.95Ca_c \) during 50 dimensionless time units (5a). Once the steady shape of \( L = 1.25 \) is attained (5b), an oscillation is imposed upon the elongation rate during 100 time units (5a). Depending upon the time scale of this oscillation, the droplet deformation will either follow this oscillation (with oscillation period \( T = 33 \)) or, when the oscillation period is increased to 50 time units, it will elongate ever faster (5d) until it deforms affinely (5c) with the continuous phase ( \( \dot{\epsilon}_d = \dot{\epsilon}_c \) ).

NON-SPHERICAL INITIAL SHAPE
Although the previous examples all started with an initially spherical droplet, no such assumptions were made while deriving the model (Stegeman et al., 1999). Actually, the model presumes an elongated droplet shape at all times. Therefore, we can investigate how the critical capillary number is influenced by a non-spherical initial shape. Again, the critical capillary number is defined as the highest capillary number where a steady droplet shape can exist, starting from the initial shape \( L_0 \) at zero capillary number and slowly increasing the flow rate.

The results are interesting. As is shown in figure 6, an initially elongated shape \( L_0 \) highly decreases the critical capillary number, especially for moderate to high viscosity ratio droplets. For low viscosity ratio droplets the influence of \( L_0 \) is negligible, since their steady state shape is always highly elongated. For high viscosity ratios, an initial aspect ratio of only 4 ( \( L_0 = 2.5 \) ) typically reduces \( Ca_c \) by a factor of 2, whereas for a thread with \( L_0 = 20 \) the critical capillary number is reduced by two orders of magnitude (note that figure 6 has a log scale).

Conclusions
The ‘initial’ droplet shape ( \( L_0 \) in figure 6) can be caused by different situations. The most obvious one is an inhomogeneous flow field. By adding a elongational flow component, even a mixing process mainly based on shear flow can cause breakup of high viscosity ratio droplets. This is easily realized in most industrial mixers (Janssen & Meijer, 1995).

Alternatively, even a time- or temperature dependent viscosity ratio of the system may result in ‘initial’ droplet shapes which are far from spherical. Consider for example a blend of two polymers with different melt- or glass transition temperature of which the dispersed phase viscosity is highly temperature
dependent, while the continuous phase viscosity hardly changes with the temperature. Starting at a low temperature, the high viscosity ratio droplet will elongate at a capillary number of about 0.2, since this is above the critical capillary number. As the temperature increases, the droplet viscosity decreases, until the viscosity ratio becomes 0.01. The capillary number of 0.2 would be insufficient to break a initially spherical droplet with this viscosity ratio. However, due to the initially high viscosity ratio, the droplet is already elongated and therefore this capillary number is sufficient to keep on stretching the droplet until it breaks. Similarly, a blend of which the droplet phase will be cured and which has a final viscosity ratio above 3.5 can be broken in simple shear, provided that the viscosity ratio remains lower until the droplet is sufficiently elongated.
References


GRACE, H. P. Dispersion phenomena in high viscosity immiscible fluid systems and application of static mixers as dispersion devices in such systems. Chemical Engineering Communications 14, 225–277 (1982).


Figure 1:
The Grace curve gives the relation between the critical capillary number $Ca_c$ and the viscosity ratio $\lambda$ for the breakup of an initially spherical droplet in quasi-steady homogeneous flow.

Figure 2:
Droplet response to a triangular flow rate - time profile where the maximum capillary number is reached in 50 (top) and 56 (bottom) seconds respectively. The average capillary number in both experiments is $0.6Ca_c$.

Figure 3:
Comparison of model predictions. On the left, the predictions for the critical capillary number and on the right the prediction of the droplet elongation rate for a droplet of viscosity ratio 0.01.

Figure 4:
Relative droplet stretching rate $\dot{\epsilon}_d/\dot{\epsilon}_c$ as a function of the relative drop length $L$ for different capillary numbers. The droplet viscosity is equal to the continuous phase viscosity.

Figure 5:
Example showing how figure 4 should be used: an initially spherical droplet with viscosity ratio 1 is subjected to time dependent velocity field. The $Ca$ - time profile shown on the top-left graph results in the droplet elongation shown in the top-right graph.

Figure 6:
Dependence of the position of the Grace curve for extensional flow on the initial droplet shape: Plotted is the critical capillary number $Ca_c$ versus the viscosity ratio $\lambda$ as a function of the initial droplet length $L_0$. 
Figure 1:

Experiments simple shear (Grace 1982)
Experiments elongation (Grace 1982)
First order theory (Taylor 1932)
Slender body: shear (Hinch and Acrivos 1979)
Slender body: elongation (Hinch and Acrivos 1980)
Figure 2:
Figure 4:

- $\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} = 1$: Affine deformation
- $\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} > 0$: Stretching of droplet
- $\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} = 0$: Steady droplet shape
- $\frac{\dot{\epsilon}_d}{\dot{\epsilon}_c} < 0$: Retraction of droplet
Figure 5:

\[ \frac{\delta \epsilon}{\delta t} = \frac{t \sigma}{R \eta} \]

\[ \frac{\delta L}{\delta t} = \frac{t \sigma}{R \eta} \]
Figure 6: