
CHEG 615 - Special Topics in Mixing

Lecture 7
Liquid-Liquid Mixing

Uses for Liquid-Liquid Mixing

- **Uses**
 - **Contacting for Mass Transfer**
 - **Single Mixer-Settler**
 - **Staged Columns**
- **Products**
 - **Stable Emulsions**
 - **Food and Cosmetic Products**

Multiphase Systems

- **Solid-Liquid**
 - Fixed Surface Area
 - Gravity plays moderate role
- **Gas-Liquid**
 - Variable Surface Area
 - Gravity plays strong role
- **Liquid-Liquid**
 - Variable Surface Area
 - Gravity plays weak role
- **Mass Transfer**
 - Similarity in mass transfer correlations

Multiphase Flow Regimes

- **Back-mixed Continuous (Liquid) Phase**
 - Solid-Liquid, Liquid-Liquid, Gas-Liquid
- **Back-mixed Dispersed Phase**
 - Solid-Liquid, Liquid-Liquid
- **Plug Flow Dispersed Phase**
 - Gas-Liquid
- **Challenges**
 - What is the interfacial surface area? $J = k_L a (C^* - C)$
 - What are the film coefficients?
- **Equilibrium Stages often used with Liquid-Liquid Systems**
 - Presumes mass transfer is fast and complete within residence time

Liquid-Liquid Drop Breakup

- **Key Principle - Drops have a characteristic strength that depends on drop size**

- characterized by

$$\frac{\sigma}{d} = \left[\frac{N \cdot m^{-1}}{m} \right] = \left[\frac{N}{m^2} \right] = \left[\frac{force}{area} \right] = [stress]$$

where σ = interfacial tension and d = drop diameter

- **In a given fluid stress field, drops will break until the characteristic strength can no longer be overcome**
 - drops break down to a maximum size beyond which they will no longer break
 - not all drops will be that maximum size
 - there will be a drop size distribution

Mass Transfer in Liquid-Liquid Systems

- **Mass Transfer Rate, J**

$$J = k_L a (C^* - C)$$

- **Average Drop Sizes**

- Various averages possible which differ bases on drop size distribution
- Sauter mean diameter, d_{32} - average of surface area per unit volume of all drops

$$d_{32} = \sum_i \frac{d_i^3}{d_i^2}$$

- **Need to estimate interfacial area, a**

$$a = \frac{6\phi}{d_{32}} \quad \text{where } \phi = \text{total volume of dispersed phase}$$

Drop Break-up in Low Viscosity Turbulent Flow

- **Drop Weber Number $(We)_d$**

- Break-up occurs above a critical $(We)_d$

$$(We)_d = \frac{\tau_c}{(\sigma/d)} = \frac{[breakup\ stress]}{[stabilizing\ stress]}$$

- **Break-up Stress in Turbulent Flow - Reynolds Stress**

$$\tau_c \propto \rho_c (u'v') \approx \rho_c (u')^2$$

- **Assume drops much larger than Kolmogoroff length scale so affected by eddies in the inertial sub-range**

$$l_E \approx \frac{(u')^3}{\varepsilon} \Rightarrow u' \approx (\varepsilon l_E)^{1/3}$$

Assume $d_{\max} = l_E$

Drop Break-up in Low Viscosity Turbulent Flow

- At drop break-up, break-up stresses balance stabilizing stresses

$$(We)_d = \frac{\tau_c}{(\sigma/d_{\max})} = \frac{\rho_c (\varepsilon d_{\max})^{2/3}}{(\sigma/d_{\max})} = const$$

$$\rho_c (\varepsilon d_{\max})^{2/3} \propto (\sigma/d_{\max})$$

$$d_{\max} \propto \left(\frac{\sigma}{\rho_c} \right)^{0.6} \varepsilon^{-0.4}$$

- ε - local power per volume not average

- In stirred tanks, use power per impeller swept volume

$$\text{Assume } \varepsilon \propto \frac{P}{\rho V_{\text{imp}}} = \frac{P_o \rho N^3 D^5}{\rho \frac{\pi D^2}{4} D_w} = \frac{P_o N^3 D^5}{\frac{\pi D^2}{4} \alpha D} = \frac{P_o}{\frac{\pi \alpha}{4}} N^3 D^2 \Rightarrow \varepsilon \propto N^3 D^2$$

- Combine to give

$$d_{\max} \propto \left(\frac{\sigma}{\rho_c} \right)^{0.6} (N^3 D^2)^{-0.4}$$

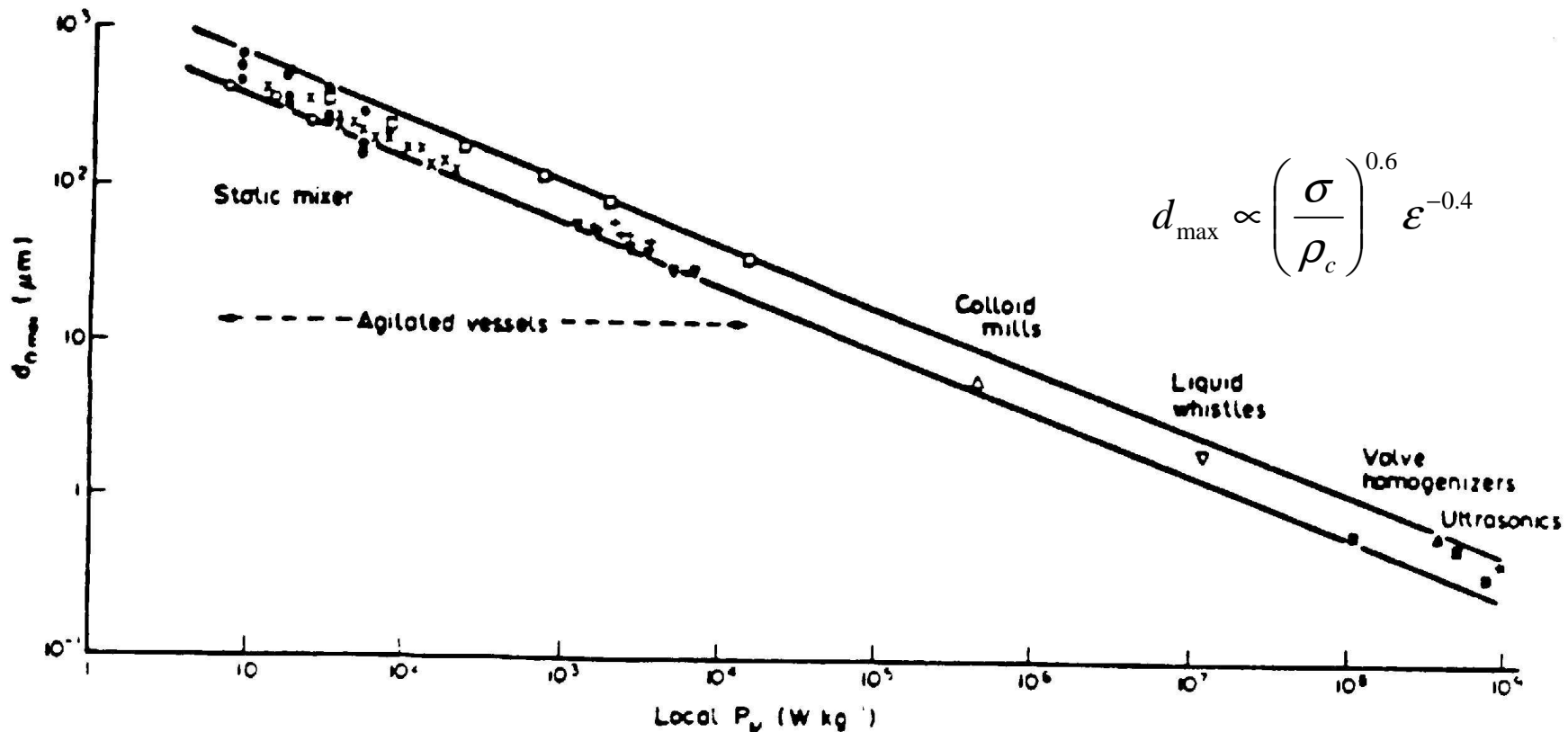
$$\frac{d_{\max}}{D} \propto \left(\frac{\rho_c N^2 D^3}{\sigma} \right)^{-0.6} \Rightarrow \frac{d_{\max}}{D} \propto (We)_D^{-0.6}$$

- Studies show $d_{\max} \propto d_{32}$ $d_{\max} = 1.7 d_{32}$ (Davies correlation)

D_{max} vs. Power per Mass

1672

J. T. DAVIES (1987)



- **Stirred Tanks may not be best for liquid drop dispersion**
 - wide distribution of eddy sizes and energy dissipation rates
 - bypassing

Equilibrium Drop Size Distribution Low to Moderate Dispersed Phase Viscosity

- **Sauter Mean Diameter including viscosity effects (Calabrese, Wang & Bryner, 1986)**

- **349 data sets (Rushton turbine)**

$$\frac{d_{32}}{D} = 0.054We^{-3/5} \left[1 + 4.42Vi \left(\frac{d_{32}}{D} \right)^{1/3} \right]^{3/5}$$

$$\text{where } Vi = \frac{\mu_d ND}{\sigma} \left(\frac{\rho_c}{\rho_d} \right)^{1/2}$$

- **Cumulative Volume Frequency (Wang & Calabrese, 1986)**

- **146 data sets**

$$F_v \left(\frac{D}{d_{32}} \right) = 0.5 \left[1 + \operatorname{erf} \left(\frac{D/d_{32} - 1.07}{0.24\sqrt{2}} \right) \right]$$

Minimum Dispersion Speed

- N_{JD} - minimum impeller speed to disperse liquid droplets
- N_{JD} Correlation for 6-blade disk impeller (Penney, et al., 1999)

$$S = \left[\left(\frac{N_{JD}^2 D}{g} \right) \left(\frac{D^2 \rho_c g}{\sigma} \right)^{1/2} \right]^{1/2} \left(\frac{\rho_h}{\rho_h - \rho_l} \right)^{1/4}$$

where

$$S = f \left(\frac{H}{Z}, \frac{C}{T}, \frac{D}{T} \right)$$

H = height of light phase in static condition, m

Z = total liquid height, m

ρ_h = density of heavy phase, kg/m^3

ρ_l = density of light phase, kg/m^3

$$\left(\frac{N_{JD}^2 D}{g} \right) = \text{Froude number } (Fr) = \frac{[\text{inertial forces}]}{[\text{gravitational forces}]}$$

$$\left(\frac{D^2 \rho_c g}{\sigma} \right) = \text{Goucher number } (Go) = \frac{[\text{gravitational forces}]}{[\text{interfacial forces}]}$$

Time to Reach Equilibrium Drop Size

- **Time to achieve equilibrium drop size**
 - long times
 - 5-20 minutes at lab-scale
 - hours at plant-scale
- **Two parallel process concept (Baladyga & Bourne)**
 - Breakup - fast process
 - Coalescence - slow process
- **Rate of Drop Break-up**
 - probability of drop going through impeller zone
 - circulation time
$$t_Q = \frac{V}{Q}$$
 - tank volume important

Coalescence - Important Factors

- **Flow field and collision rate**
- **Volume fraction of the dispersed phase**
- **Viscosity of both phases**
- **Condition, age, viscosity and mobility of drop interfaces**
- **Presence of particulates, surfactants or suspending agents**
- **Coalescence can occur at many locations which complicates interpretation**
 - **impeller blades**
 - **baffles**
 - **liquid surface**

Population Balance Equation

$$\begin{aligned} \frac{\partial}{\partial t}[N(t)A(v, t)] &= \int_v^{v_{max}} \beta(v', v)\nu(v')g(v')N(t)A(v', t) dv' \\ &- g(v)N(t)A(v, t) \\ &+ \int_0^{v/2} \lambda(v - v', v')h(v - v', v')N(t)A(v - v', t)N(t)A(v') dv' \\ &- N(t)A(v, t) \int_0^{v_{max}-v} \lambda(v, v')h(v, v')N(t)A(v', t) dv' \end{aligned}$$

- $N(t)$ = total number of droplets in the vessel at time t
 $A(v, t)$ = number probability density for drops of volume v at time t
 $\beta(v', v)$ = breakage kernel; the number probability density of daughter drops of volume v formed by the breakup of a parent drop of volume v'
 $\nu(v')$ = mean number of daughter drops resulting from breakage of a parent drop of volume v'
 $g(v')$ = breakage frequency of a drop of volume v'
 $\lambda(v, v')$ = collision efficiency of drops of volume v with drops of volume v'
 $h(v, v')$ = collision frequency between drops of volume v and drops of volume v'

Separator (Decanter) Design

- **Liquid-liquid Flow into a Cylindrical Vessel**
- **Quiet Zone where interface forms**
- **Coalescence Layer or Band**
- **Assume drops in both phases**
- **Settle to coalesce and form interface**
- **Avoid interfering with settling process**
 - Gravity separation
 - Settling rate given by Stoke's Law

$$V_s = d^2 \left(\frac{\rho_c}{\rho_d} \right) \frac{18g}{\mu_c}$$

- **Design for a certain cut size**
 - for instance, get all drops above 125 microns
- **Keep (through flow)/(velocity) equal to cut size settling rate**