Mixing Science and Practice – A Reflective View

VisiMix Conference

October 20-22, 2014

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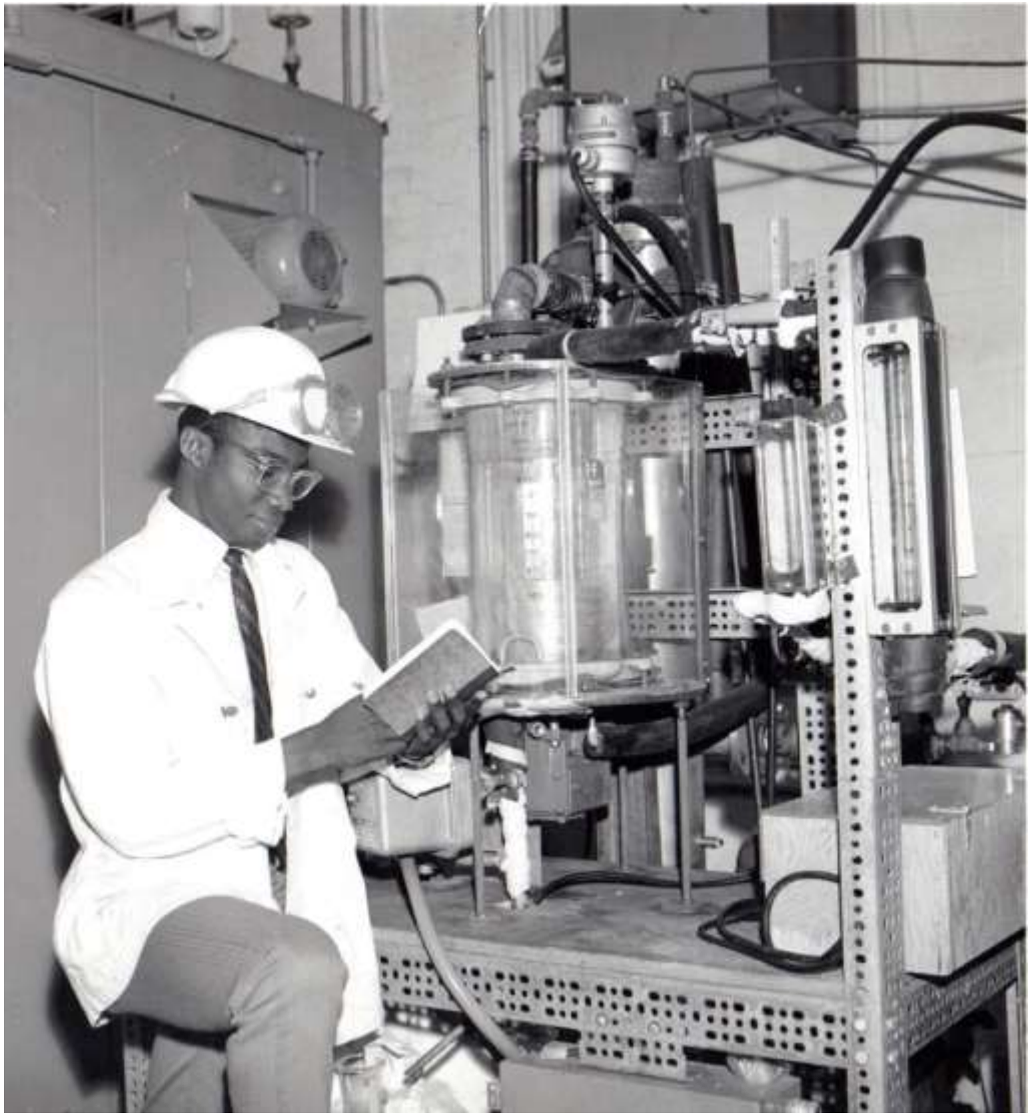
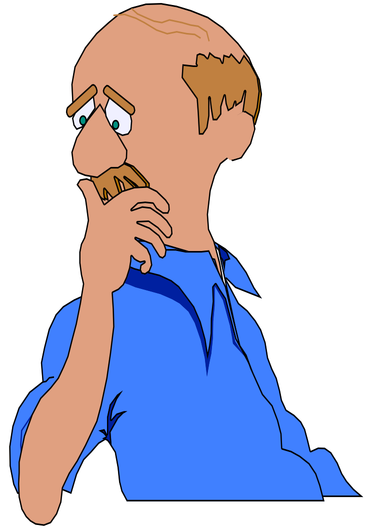
Retiree from The Dow Chemical Company

A look back

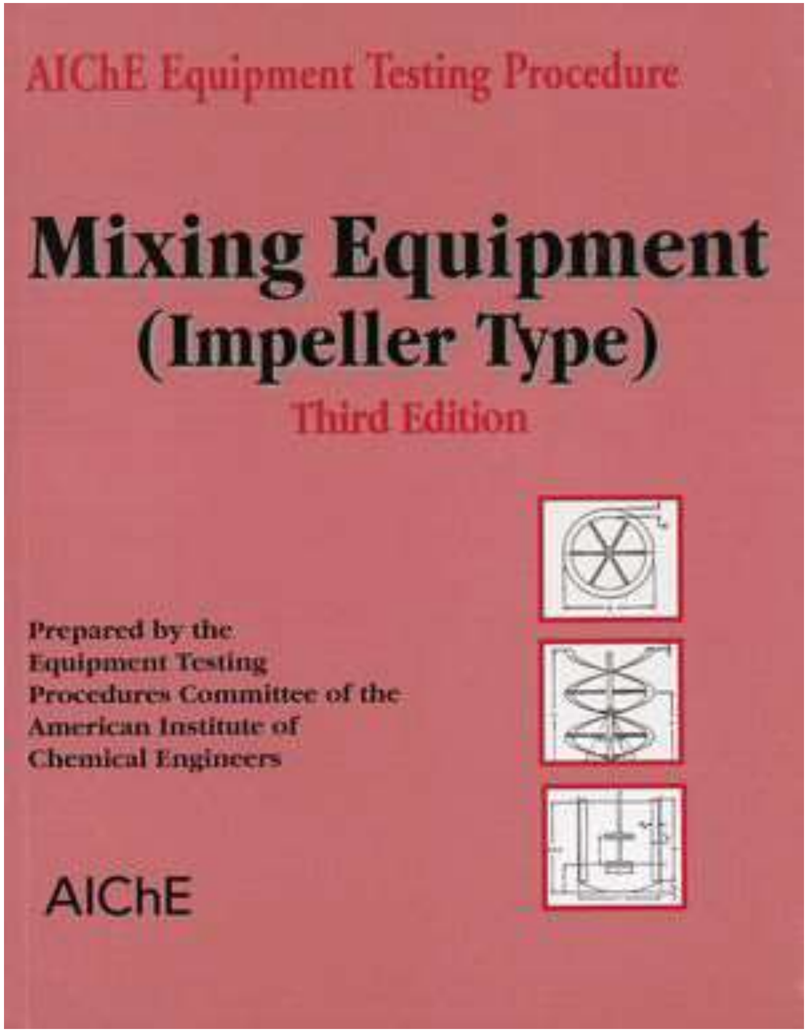




- Summer of 1970
- Crystallization of Epsom Salt
- Most effective cooling profile for maximum crystal yield per batch

Mixing not mentioned!

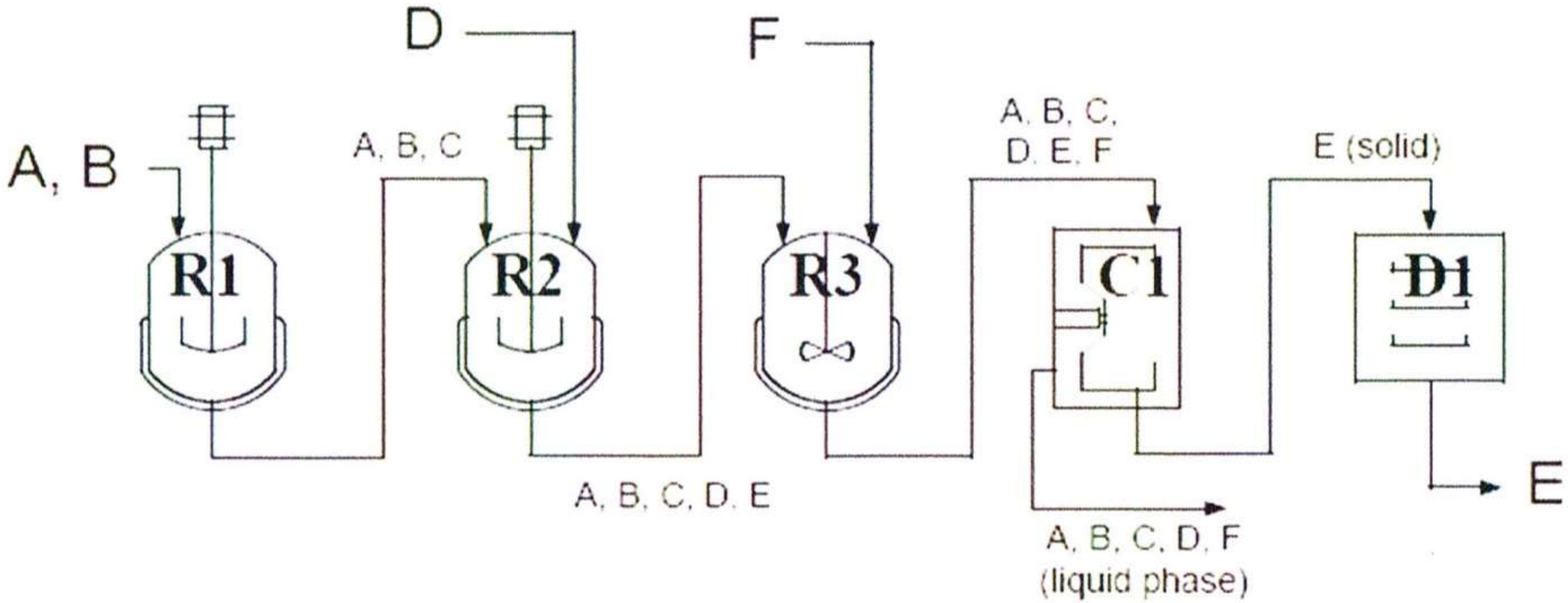
Fast forward to 2001



Dickey, D., et al (*2001)* ***AIChE Equipment Testing Procedure - Mixing Equipment (Impeller Type), 3rd Edition***

Fast forward further to 2003

Chemical & Allied Processing Industries



Blend reagents A and B Heat and React to form C Transfer to R2	*Blend in reagent D React with C to form E*	*Blend in reagent F Cool and crystallize E*	*Separate E by centrifuge*	*Dry E*

Effective mixing is required for success

Mixing - The Forgotten Unit Operation

“Although mixing equipment appears in nearly every process plant, mixing as a discipline is not routinely taught to undergraduates …”

CANADIAN J. OF CHEMICAL ENGINEERING, VOL. 89, OCTOBER 2011 p959

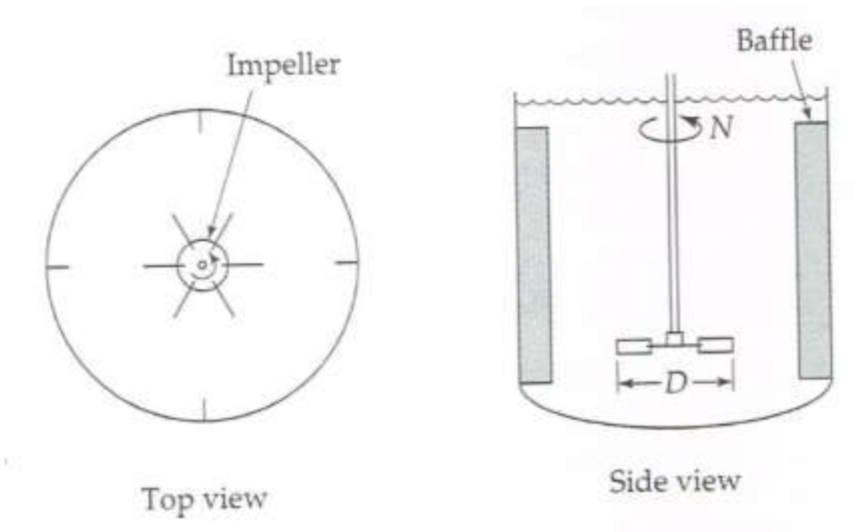
What was your academic exposure to mixing concepts?

Ideal reactors in Reaction Engineering

- uniform concentration and other properties
- instantaneous change in response to change

Power correlation for agitated/stirred tank

$$Np \equiv \frac{P}{\rho N^3 D^5} = \Phi\left(\frac{(ND)D}{\upsilon}, \frac{N^2 D}{g}, Nt\right)$$



Np, Power Number [-]
P, Power input [W]
N, Impeller rotation [s-1]
D, Impeller diameter [m]
T, Time from start [s]
g, Gravitational acceleration [m2/s]
ρ, Density [Kg/m3]
ν, Kinematic viscosity [m2/s]

Bird, Stewart and Lightfoot, *Transport Phenomena, Wiley 1960, p. 205*

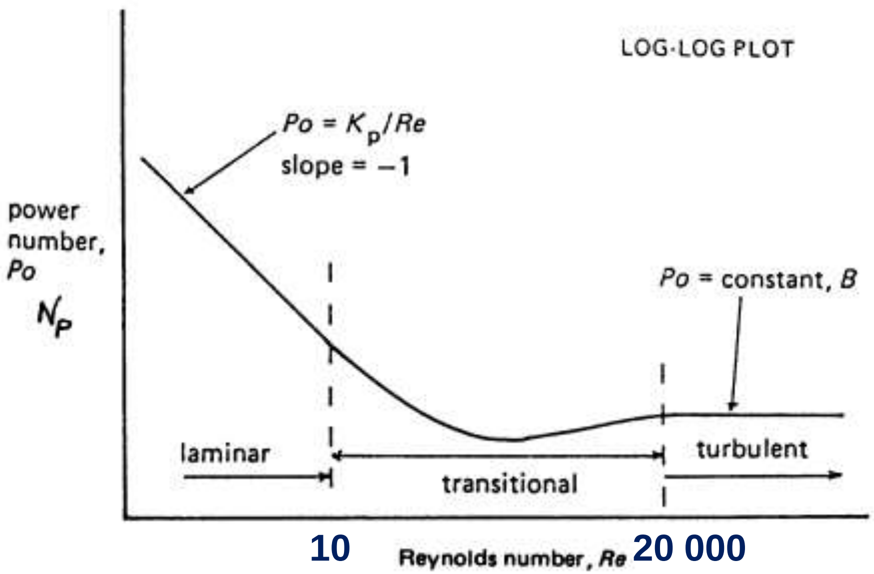
Power correlation for agitated/stirred tank

Power Number and Flow Regimes

- Laminar: Re< 10
- Turbulent: Re> $2x10^4$
- Transitional: $200<Re<2x10^4$

$$Re = \frac{ND^2}{\nu}$$

$$P = N_P \rho N^3 D^5$$



Stirred Tank Hydrodynamics: Laminar or Turbulent flow?

***Hydrodynamic Regime characterized by Reynolds Number,* Re$_l$**

$$Re_l = \rho(ND)D/\mu$$

Characterized by Reynolds Number, Re$_l$

Depends on -

- *fluid properties: density,* ρ; *viscosity,* μ
- *size or scale of equipment: impeller diameter, D*

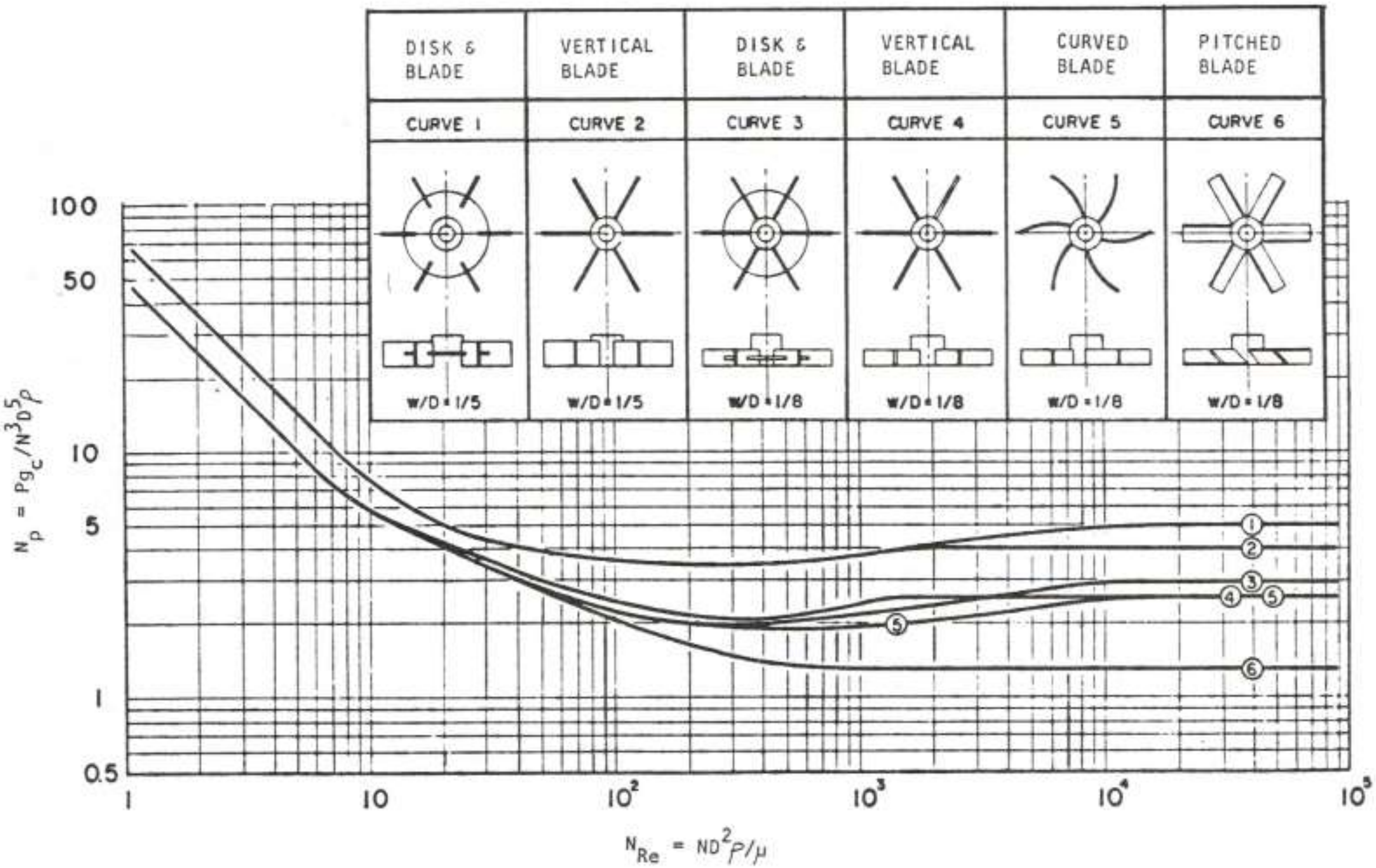
Consequences -

- *Mixing mechanisms are different*
- *Equipment requirements differ*

ViSiMiX software for chemical engineering

Power correlation for agitated/stirred tank

Landmark paper

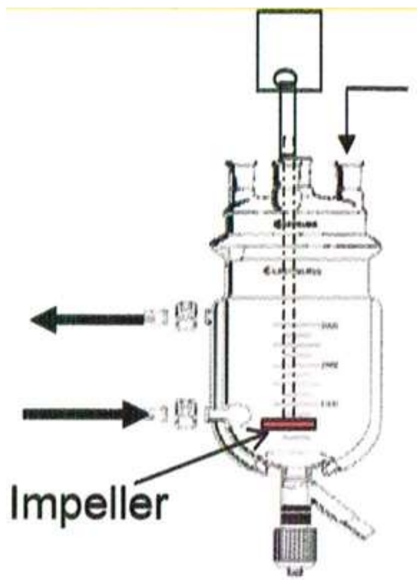


Bates, Fondy and Corpstein, *Ind. Eng. Chem. Process. Des. Dev. 2(4) 311 1963*

My introduction to industrial mixing science and practice

1983/4

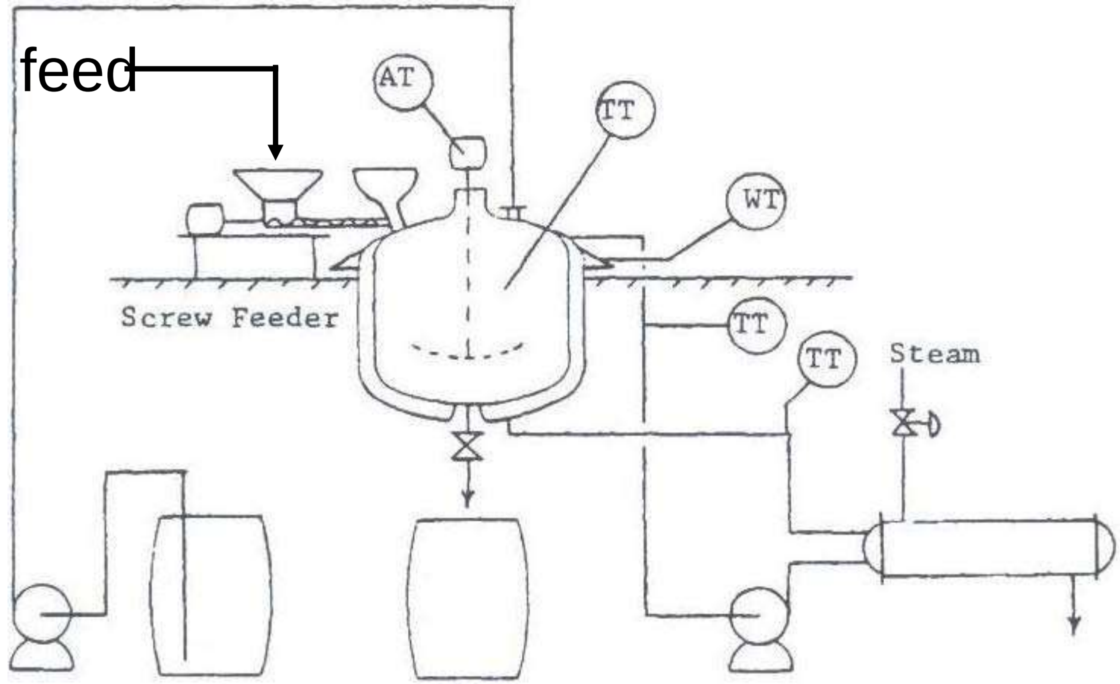
Scaling-up $MM herbicide solid-liquid reaction process



Solid feed

Lab

Solid feed



Pilot plant

From solvent process to solvent-less process

- Lab studies of effect of stirrer speed
- Solid reagent addition rate
- Fluid: slurry viscosity – low -> high -> low
- 2nd dense liquid phase forms towards end of reaction

Typical Mixing Scale-up rules

Scale-up index ND^X	Scale-up Rule	Process application
X=1	Constant tip speed; constant torque/volume	simple blending
0.85	Just suspended solids	Zweitering correlation for just suspension speed
0.67	Constant power/volume	Fast settling solids; gas-liquid mass-transfer
0.5	Constant Reynolds Number	Constant heat transfer
0	Constant speed	Equal mix time

Mixing Scale-up dilemma

Mixer performance function	Pilot scale 20 gal	*Plant scale 2500 gal* Case 1	Case 2	Case 3	Case 4
Impeller diameter, D	**1**	**5**	**5**	**5**	**5**
Impeller speed, N	1	**1**	0.34	0.2	0.04
Impeller tip speed, ND	1	5	1.7	**1**	0.2
Impeller power, P	1	3125	125	25	0.2
Impeller power/volume	1	25	**1**	0.2	0.0016
Impeller generated flow rate, Q	1	0.25	42.5	25	5
Impeller generated flow rate/volume	1	**1**	0.34	0.2	0.04
Reynolds number, Re	1	25	8.5	5	**1**

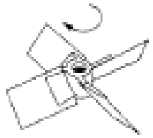
J. Oldshue

Typical power requirement for stirred tank operations

Power Level	Mixing Objective	Approx. Specific Power (W/kg)
Low	Suspend light solids; Blend low viscosity liquids	0.2
Moderate	Some heat transfer; Gas-liquid dispersion; Liquid-liquid contact; Suspend moderate density solids	0.6
High	Suspend heavy solids; Emulsification; Gas-liquid dispersion	2
Very High	Blend high viscosity paste, dough, etc.	4

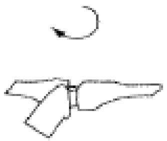
Standard Impeller types

Propeller

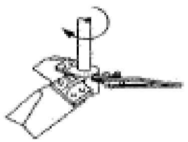


Pitched blade turbine

- Axial impeller: good pumping rates
- *Blending, solid suspension*

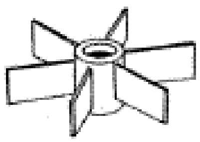


Lightnin A310

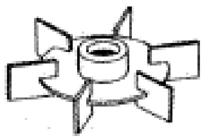


Chemineer HE3

- Hydrofoil impeller: high pumping rates
- *Blending, solid suspension*

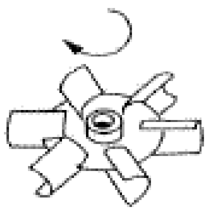


Open Flat Blade



Disk Style (Rushton)

- Radial impeller: high local turbulence
- *Liquid-liquid & Gas dispersions*



Scaba SRGT
Chemineer CD6

- Radial impeller
- *Gas dispersion - high gas flow*

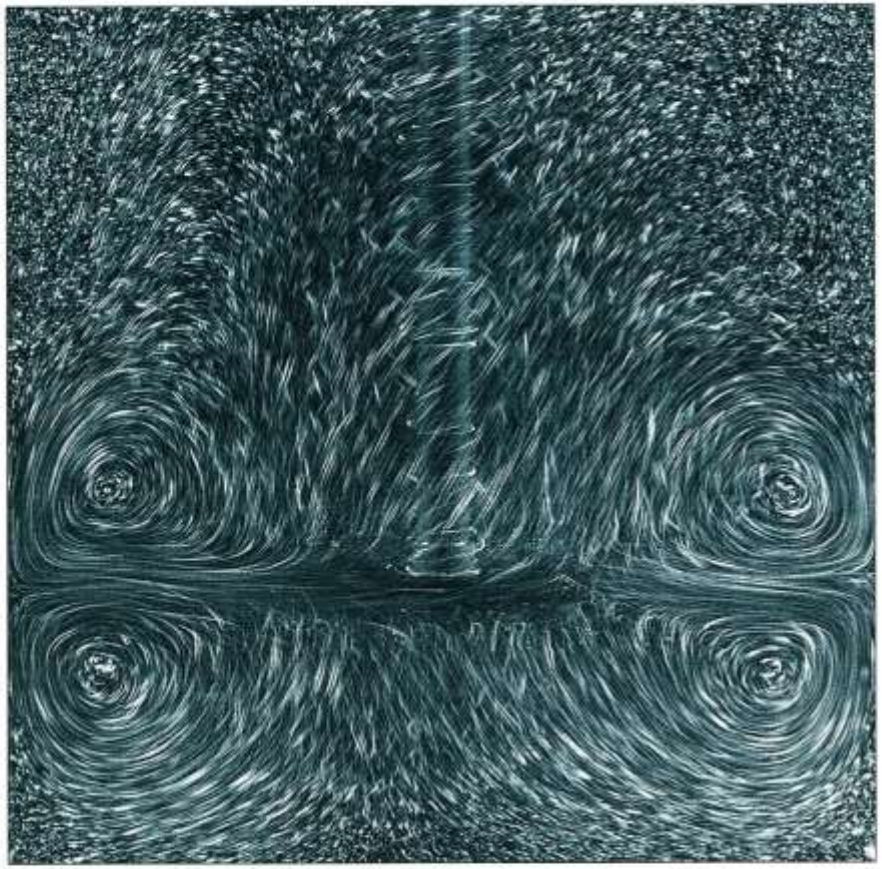
Helical ribbon

Paravisc

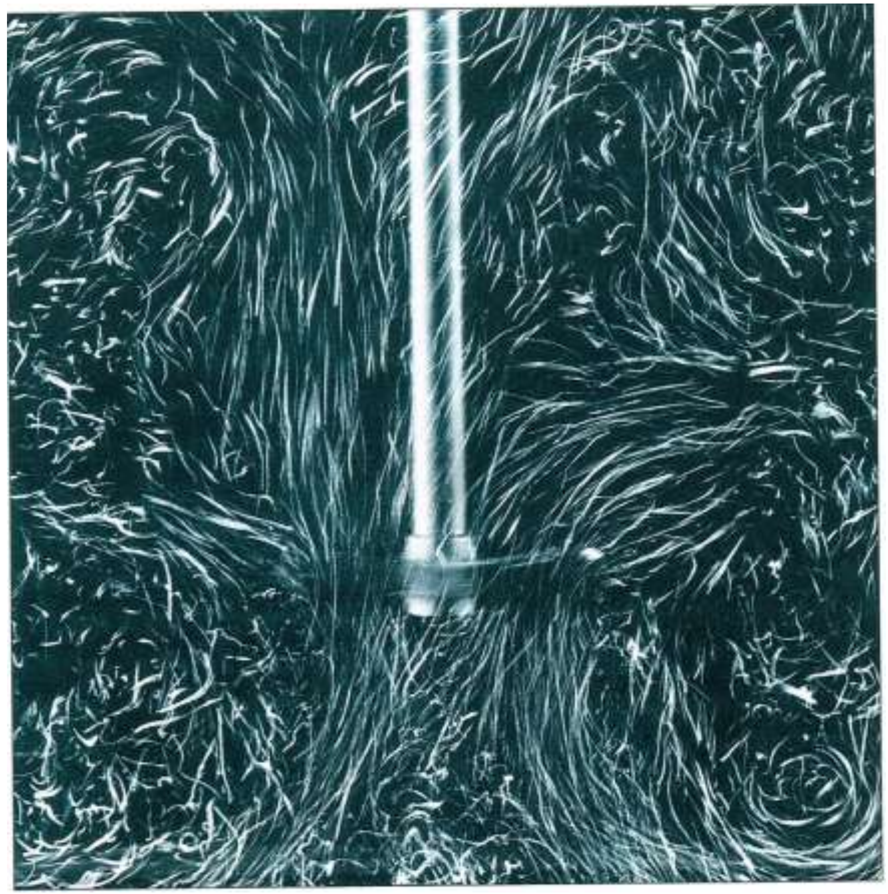
- Proximity impellers
- *Laminar or high viscosity processes*

Flow patterns in stirred tanks

Laser light section of flow patterns in agitated /stirred tank



Radial



Axial

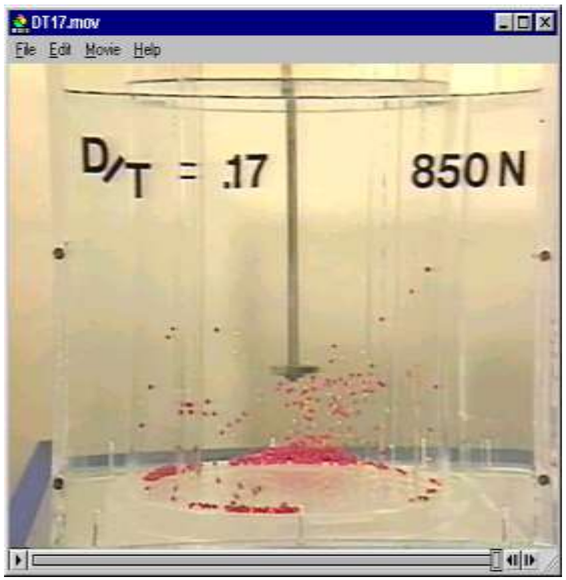
Ekato Handbook of Mixing Technology, 1990; 2000

Hydrodynamics of Solid-liquid Mixing

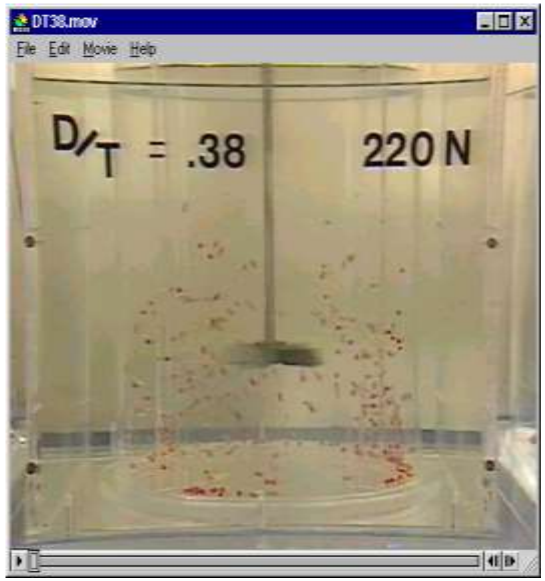
An eye opening experiment

$$P = Po \rho N^3 D^5 \qquad Tq = P / 2\pi N$$

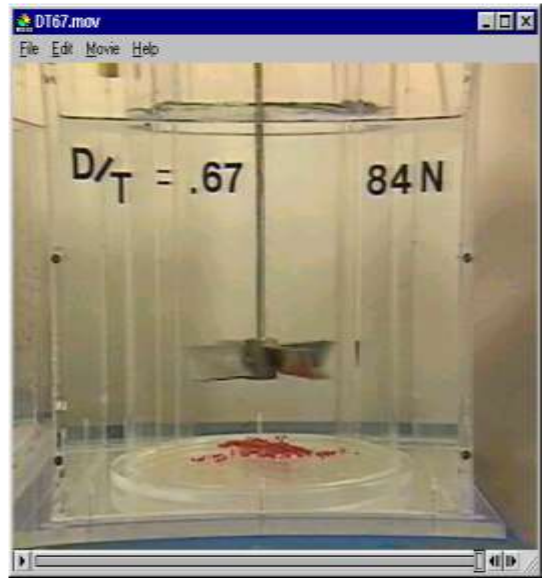
Relative P=1
Relative Tq=0.3



Relative P=1
Relative Tq=1



Relative P=1
Relative Tq=3



Courtesy of Lightnin

In-house Mixing Expertise Development

- 1984: Successfully scaled-up solid-liquid reaction process for $$MM herbicide plant
- 1984: Organized in-house mixing seminar
  - Presentation: "Elements of Mixer Selection, Scale-up and Design –All I Know About Mixing"
  - Named Process Engineering Subject Matter Expert - Mixing
- 1989: 1st Engineering Foundation Mixing Conference, Potosi, MO
  - Invited by Ed Paul to chair session on Viscous Mixing
- 1989-1995: In-house Introductory Mixing Course: "Elements of Mixer Selection, Scale-up and Design"
- 1992-94 Dow Mixing Manual/Dow Mixing Courses

Industrial Mixing Expert

The surest way to be an expert in something is to have the passion to

Learn
Apply
Document
Teach

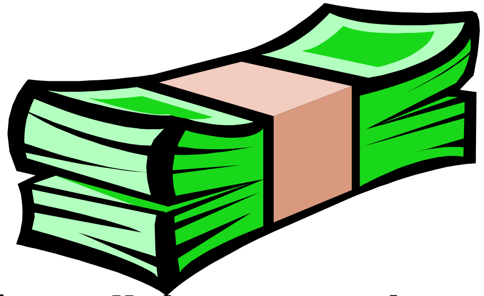
Dow Mixing Manual Team 1992-1994

TRAINING PROCESS

Emphasize

- ***Role and Importance of Mixing***
- ***Key Concepts of Mixing***
- ***Common Mixing Operations***
  - ***Underlying physical principles***
  - ***Scale-up/Scale-down & Design aspects***
- ***Hardware***
  - ***Design features***
  - ***Performance characteristics***
  - ***Application ranges***

IMPORTANT LESSONS



Process failure *from "**inadequate mixing**" is costly*

- lower reaction yields, more by-product formation
- longer reaction/process times
- unacceptable product properties
- higher costs for purifications, waste handling, etc.
- higher production costs for product rework, etc.
- less safe operations

Early and careful assessment of effect of mixing on process is imperative!

In-house perspective & support

Appreciation at the highest levels of the value of effective mixing demonstrated by

Investment in mixing resources

- *Well equipped laboratories*
- *Computational productivity tools -*
- *Enlightened employees (R&D, Engineering, Manufacturing)*
- *Membership and participation in relevant mixing research consortia*

In-house perspective & support

Relevant mixing research consortia

- British Hydromechanics Research Group (BHRG) Cranfield, UK
- High Shear Mixing Research Consortium, Rich Calabrese @ U of Maryland
- Consortium on Innovative Mixing Process Models for Highly Rheologically Complex Media, Philippe Tanguy @ Ecole Polytechnique, Montreal

In-house vision

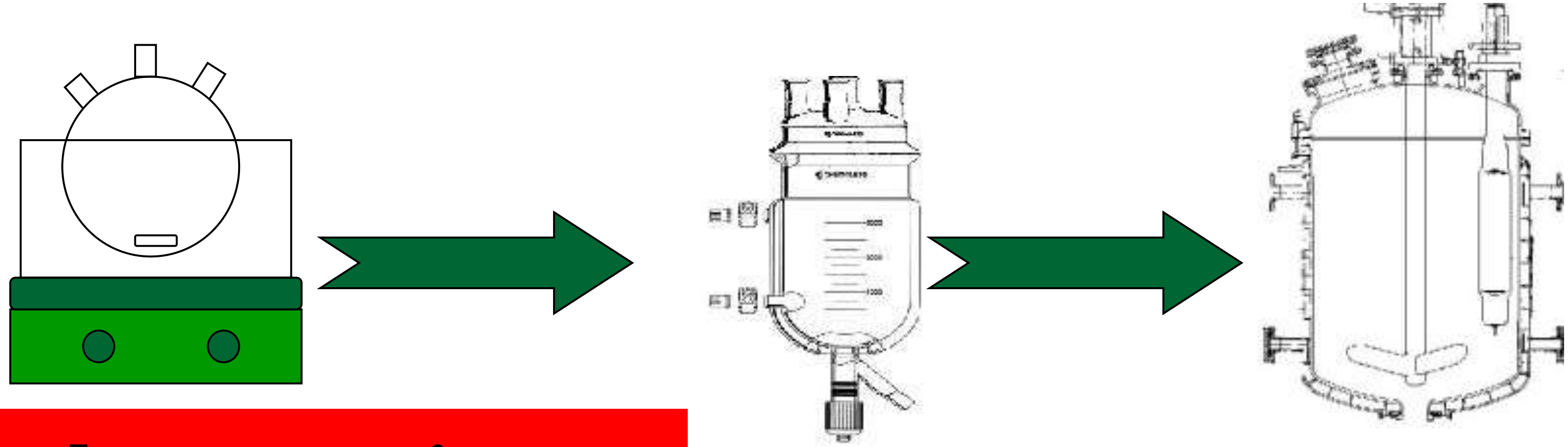
- Appreciation of the value of effective mixing is widespread
- Mixing expertise is broadly distributed
- Mixing experts are engaged early in process research and development to address relevant & tough problems
- Design is based more on understanding the relevant underlying physico-chemical phenomena of the process
- Appropriate use of the relevant tools for the correctly identified problems

IMPORTANT LESSON

"Fundamental knowledge must be coupled with practical insight and engineering judgment to solve problems associated with real industrial applications"

Leng & Calabrese (2004) ***in Handbook of Industrial Mixing: Science and Practice,*** **Eds. E.L. Paul, V.A. Atiemo-Obeng and S.M. Kresta, Wiley & Sons.**

Chemical Process Development & Scale-up



Physical properties

- Phases
- Density
- Viscosity & rheology

Chemistry

- Chemical equilibria
- Chemical kinetics

Transport phenomena

- *Hydrodynamics/Mixing*
- Mass transfer
- Heat transfer

Describing mixing in batch processes

Consider these cases:

- *Prepare a drink: Rum and Coke*
- *Sweeten tea/coffee with honey or granular sugar*
- *Make salad dressing: Oil and vinegar*
- *Make bread dough: flour and water*




Describing mixing in batch processes

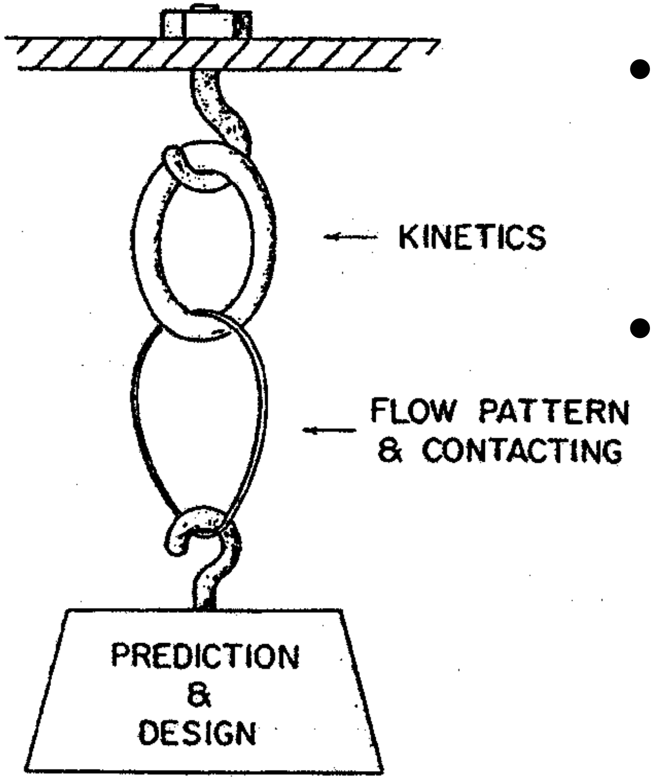
Consider these cases:

- ***Prepare drink: Rum and Coke***
- ***Sweeten tea/coffee with honey or granular sugar***
- ***Make salad dressing: Oil and vinegar***
- ***Make bread dough: flour and water***

Compare based on:

- Desired process outcomes
- Phases involved
- Phenomena occurring
- Difficulty/challenge
- Equipment used

Process Development, Scale-up and Design: Role of Hydrodynamics



- *Kinetics and hydrodynamics required for reactor scale-up & design*

- *"Often, the lack of knowledge of the **expected flow pattern** in the reactor is the **main cause of uncertainty** in the design of reactors, **not the kinetics**."*

  Levenspiel (1999) Ind. Eng. Chem. Res. 38, 4140

Effective stirring producing desired hydrodynamics is required for success

Hydrodynamics and Mixing

*Mixer converts mechanical energy into kinetic energy to induce **hydrodynamics environment***

- ***Bulk or macro-flow***
- ***Micro-flow** - turbulent eddies …*
- ***Shear Strain & Stress***

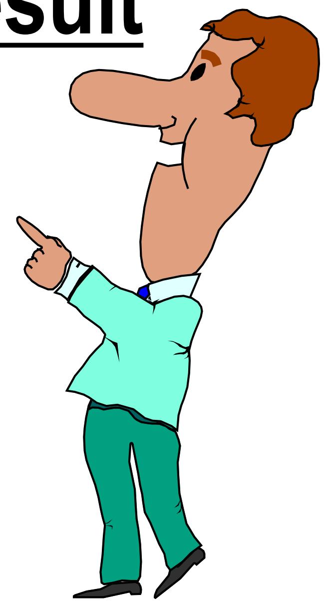
Challenge:

Understand the required hydrodynamics environment <u>and</u> select/ design mixer to create it!

Goal: Use energy efficiently to create the appropriate Hydrodynamic environment

Defining Mixing

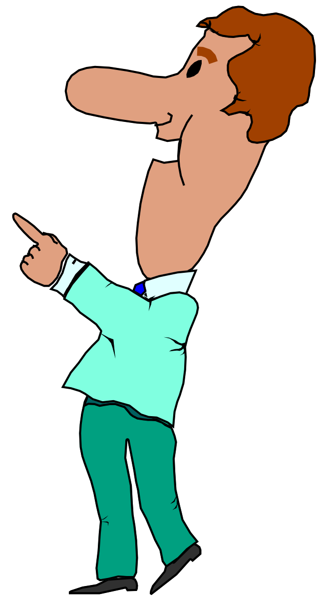
Process operation where **mechanical energy induces fluid motion in a volume of fluid** in order to **reduce inhomogeneities of the fluid's properties to achieve a <u>desired process result</u>**



Purpose of Mixing

Affect a process in a desired manner:

- ***Blend miscible fluids to make concentration, temperature more homogeneous***
- ***Enhance chemical reactions and control reaction selectivity***
- ***Suspend solids in a liquid***
- ***Create a dispersion of liquid in another (oil/water)***
- ***Disperse a gas in liquid***
- ***Enhance heat or mass transfer***



Mixing Processes

Primary Category	Sub-categories	
Miscible Phases blending with/without reactions	• Blending fluids with similar properties (density, viscosity, etc) ▪ Processes with varying mixture viscosity and rheology	▪ Blending fluids with dissimilar properties ▪ Blending small amounts of low viscosity fluid into high viscosity bulk fluid
Multi-phase fluids with/without reactions	▪ Solid dissolution ▪ Solid-liquid slurries ▪ Incorporation/dispersion of powders & nanomaterials ▪ Dispersing/activating clays ▪ Liquid-liquid dispersions ▪ Gas-liquid dispersions	▪ Crystallization ▪ Precipitation reactions ▪ Extractions ▪ Emulsion polymerization ▪ Suspension polymerization ▪ Heating/Boiling fluids

Challenging Mixing Processes requiring closer careful attention

Blending

- ***Higher density, higher viscosity miscible liquid into thin bulk***
- ***Blending/reacting as viscosity increases and rheology changes***
- ***Incorporation, dispersion, dissolution of powders into viscous bulk***

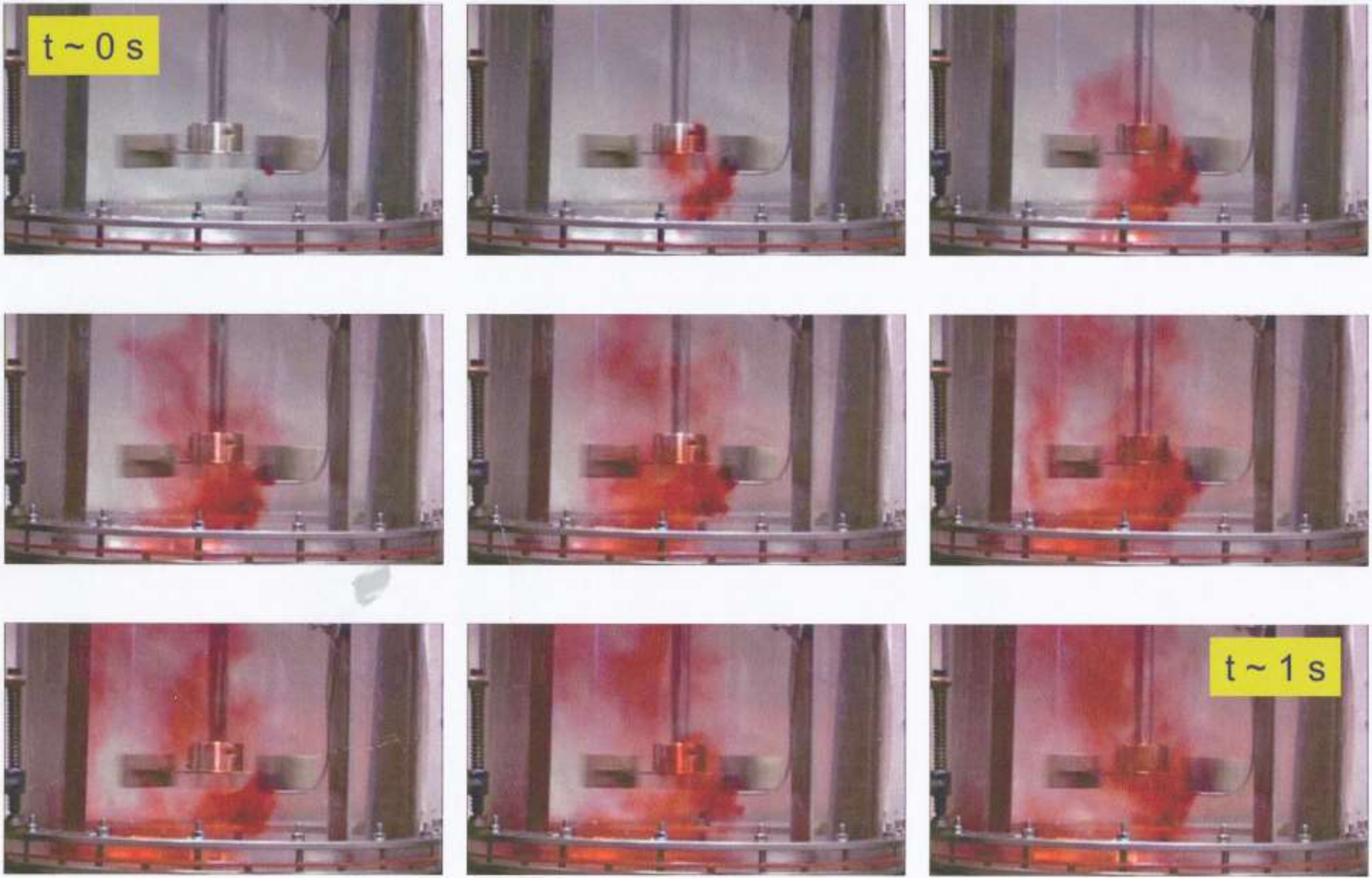
Solid-Liquid

- ***Incorporating / dispersing poor wetting solids into liquid***
- ***Agglomeration of polymer pellets during dissolution***
- ***Achieving suspension of fragile needle-shaped crystal with minimal attrition***
- ***Settling and packing of solids on vessel bottom***
- **Encrustation on wetted surfaces during crystallization or precipitation**

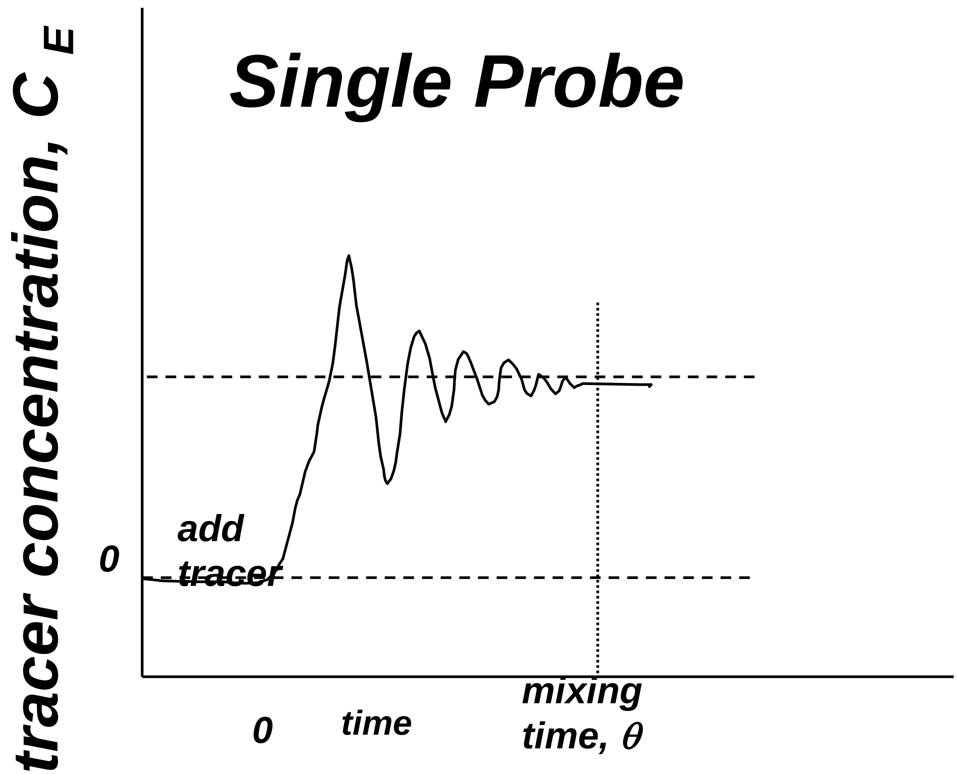
Liquid-liquid

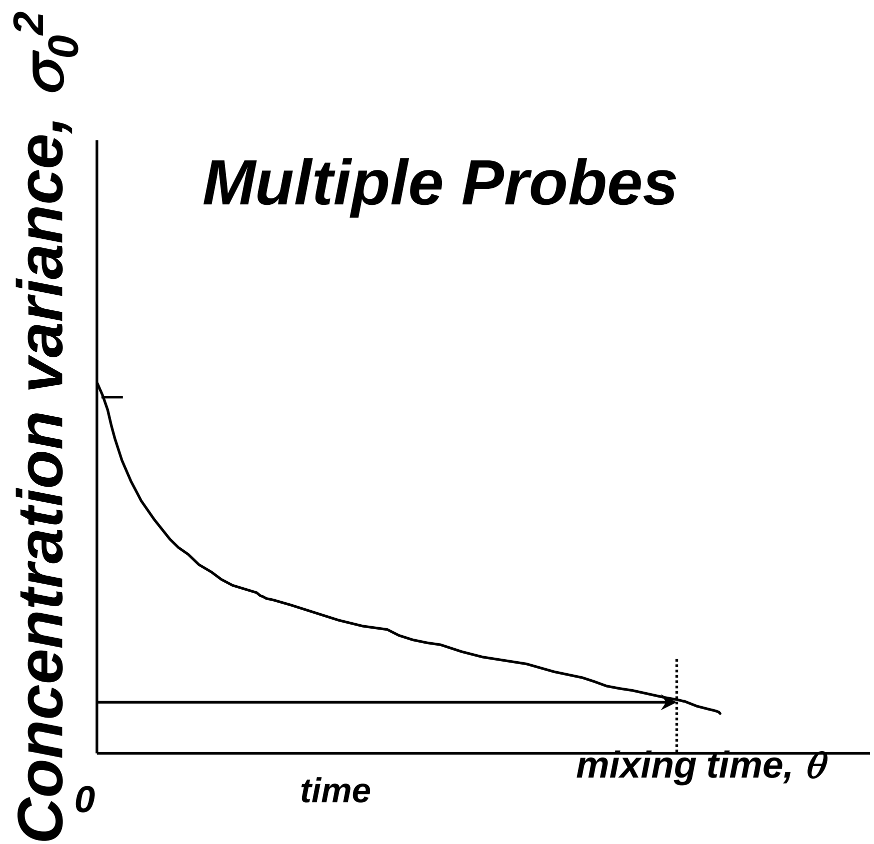
- ***Drop size prediction for concentrated & surfactant laden dispersions***
- ***Catastrophic phase inversion during formulation***
- ***"Fouling" or gel formation in emulsion polymerization***

Miscible liquid blending phenomena



Miscible liquid blend time determination





$$\sigma^2 = [1/(n-1)] \sum_{i=0}^{n} (C_i - C_E)^2$$

Where, C_E *= equilibrium concentration,*

C_i *= concentration at time t recorded by the ith detector*

n *= number of detectors in the working media*

Miscible liquid blending phenomena in poorly baffles tanks

No Baffles	2 Flat	2 Beavertails	2 Cylindrical

Injection Point

Flow patterns and region of last color change

Baffled cases had similar mix times

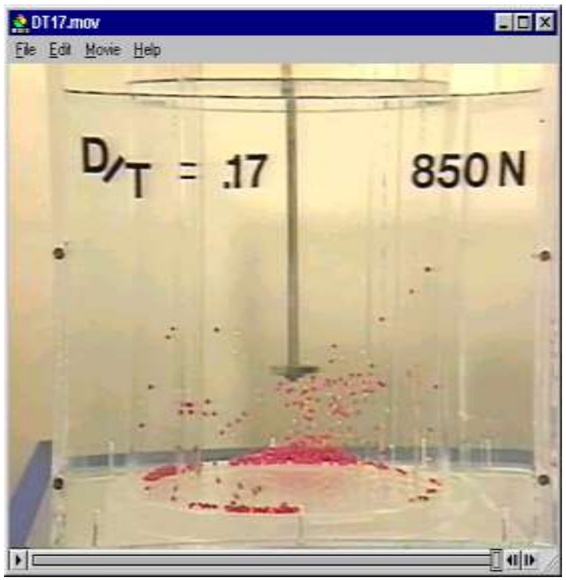
2006 AIChE Annual Meeting, Presentation 506b

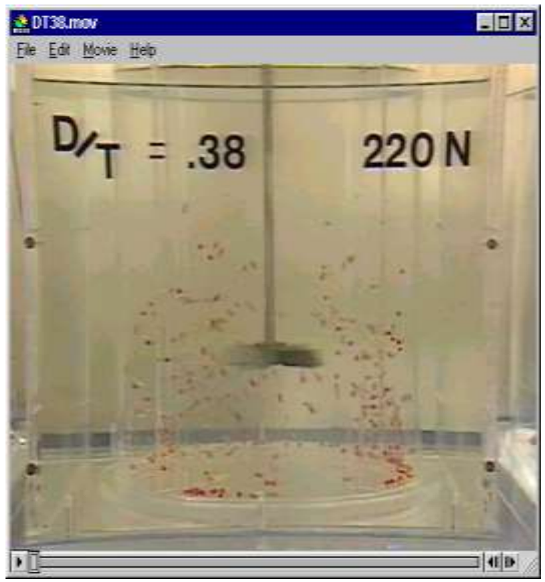
Hydrodynamics of Solid-liquid Mixing

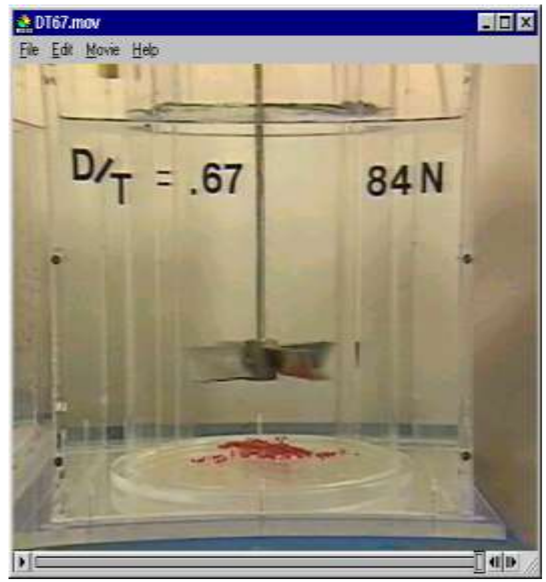
An eye opening experiment

$$P = Po \rho N^3 D^5 \qquad Tq = P / 2\pi N$$

Relative P=1	Relative P=1	Relative P=1
Relative Tq=0.3	Relative Tq=1	Relative Tq=3







Courtesy of Lightnin

Hydrodynamics of Solid-liquid Mixing: Key phenomena

Dense solid particles

- ***Suspension:***

  Particle pick-up from vessel base

- ***Distribution:***

  Circulation by large-scale fluid motions

Light solid particles

- **Wetting:**

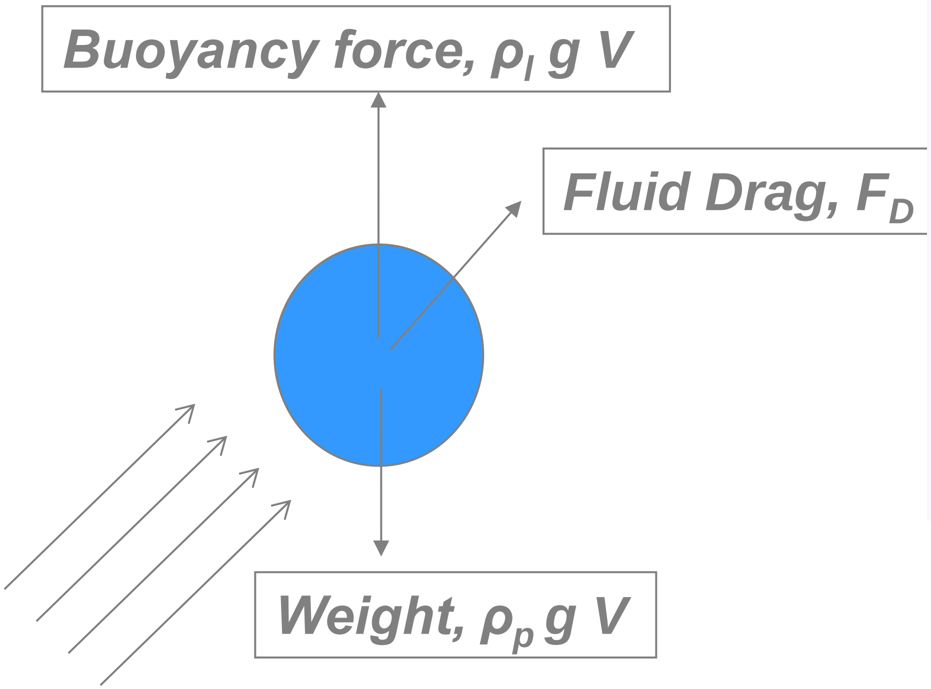
  Spreading of liquid over surface of solid

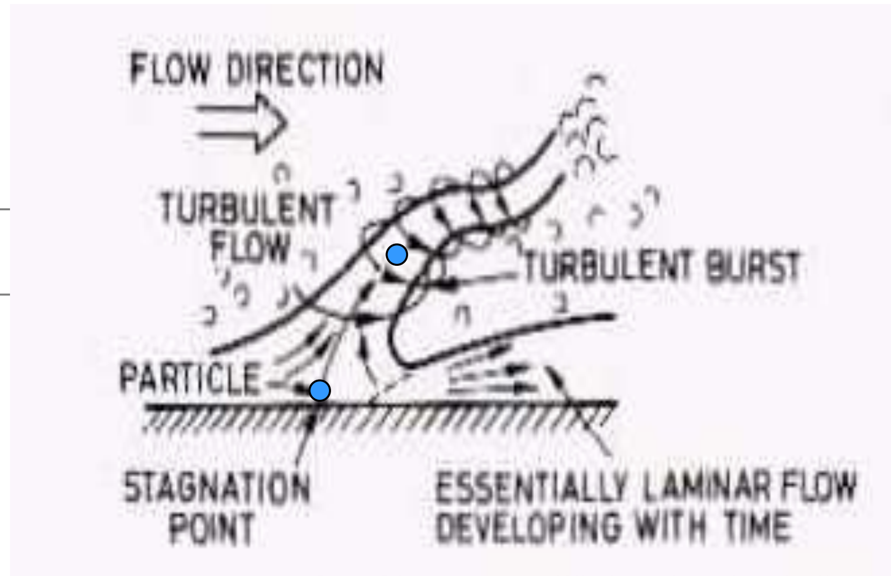
- **Drawdown:**

  Particle pull-down from liquid surface

Hydrodynamics of Solid-liquid Mixing: Key phenomena

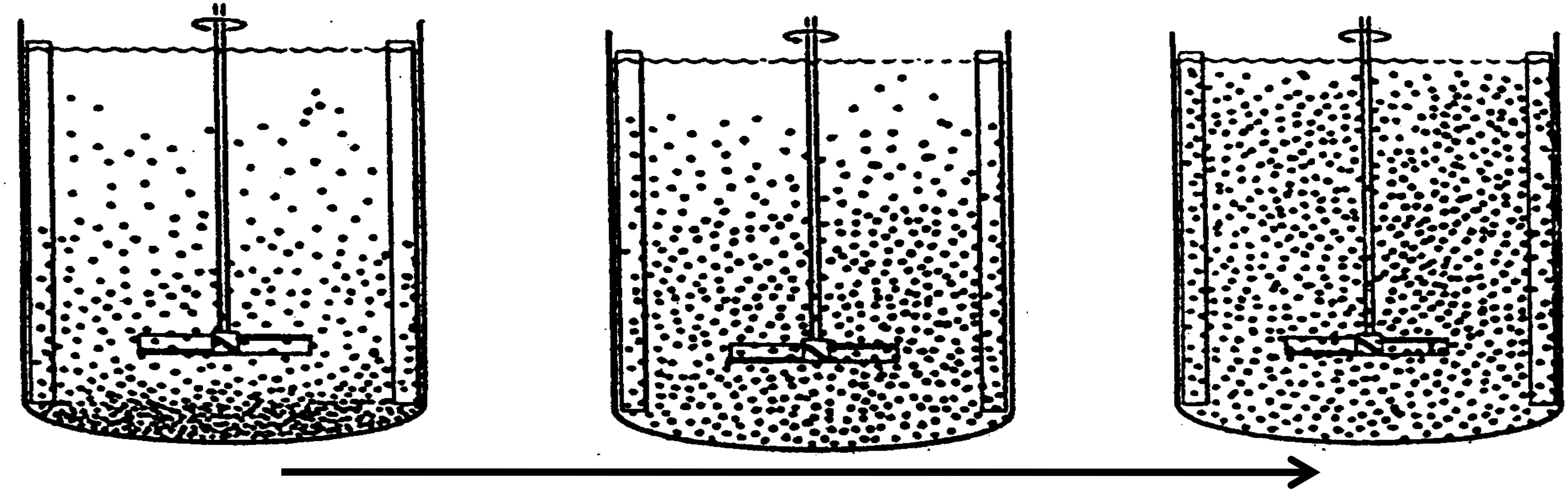
Forces on Suspended Particle





Schematic representation for particle pick-up from vessel base (Cleaver & Yates,1973)

Hydrodynamics of Solid-liquid Mixing: Levels of suspension



Increasing impeller rotational speed, N

Partial Suspension

- *some solids rest on bottom of tank for short periods*
- *acceptable for dissolution of very soluble solids*

Complete Off-Bottom/ "Just Suspension"

- *no solids rest on bottom from more than a few seconds*
- *minimum condition for most applications*

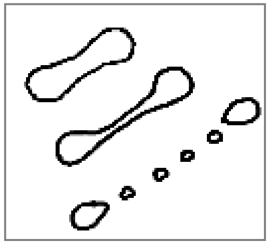
Uniform

- *solids uniformly distributed*
- *required for crystallization, slurry feeds, etc.*

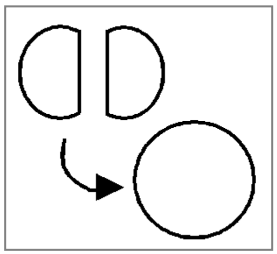
Liquid-Liquid Dispersion Phenomena

Liquid draw down

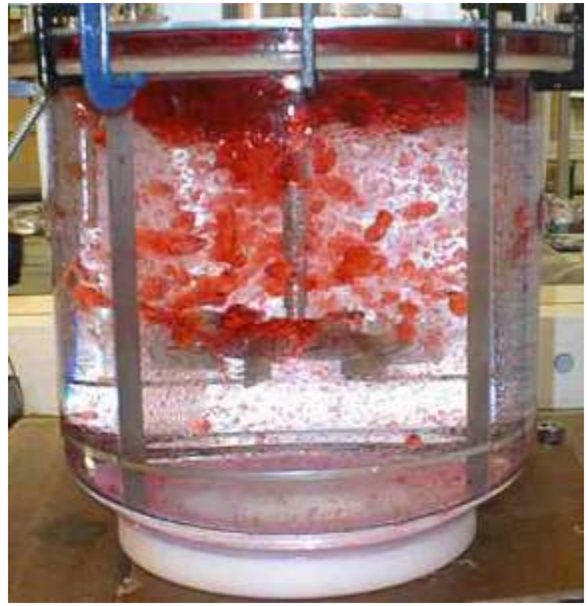
Drop break-up



Drop coalescence



Drop suspension / distribution



Liquid-Liquid Dispersion Phenomena

- Drop break-up and dispersion
  - Requires threshold energy
  - Easier with bigger drops
  - Facilitated in liquids with
    - lower viscosities
    - Lower interfacial tension by use of surface active agents – surfactants, stabilizers
- Drop coagulation/coalescence and aggregation
  - Influenced by energy input, continuous phase viscosity, dispersed phase volume fraction, drop size
- Suspension of drops
  - Influenced by phase density difference, energy input, impeller type/size/location, continuous phase viscosity, dispersed phase volume fraction, drop size
- Type of dispersed phase (w/o, o/w)
  - Bancroft rule: surface active agents promote dispersion of phase with lower solubility
- Interfacial science: adsorption and diffusion of surfactants and other surface active components at interface:
  - Surfactants/emulsifiers/suspending agents reduce interfacial tension, affect surface mobility
  - Stabilize dispersions

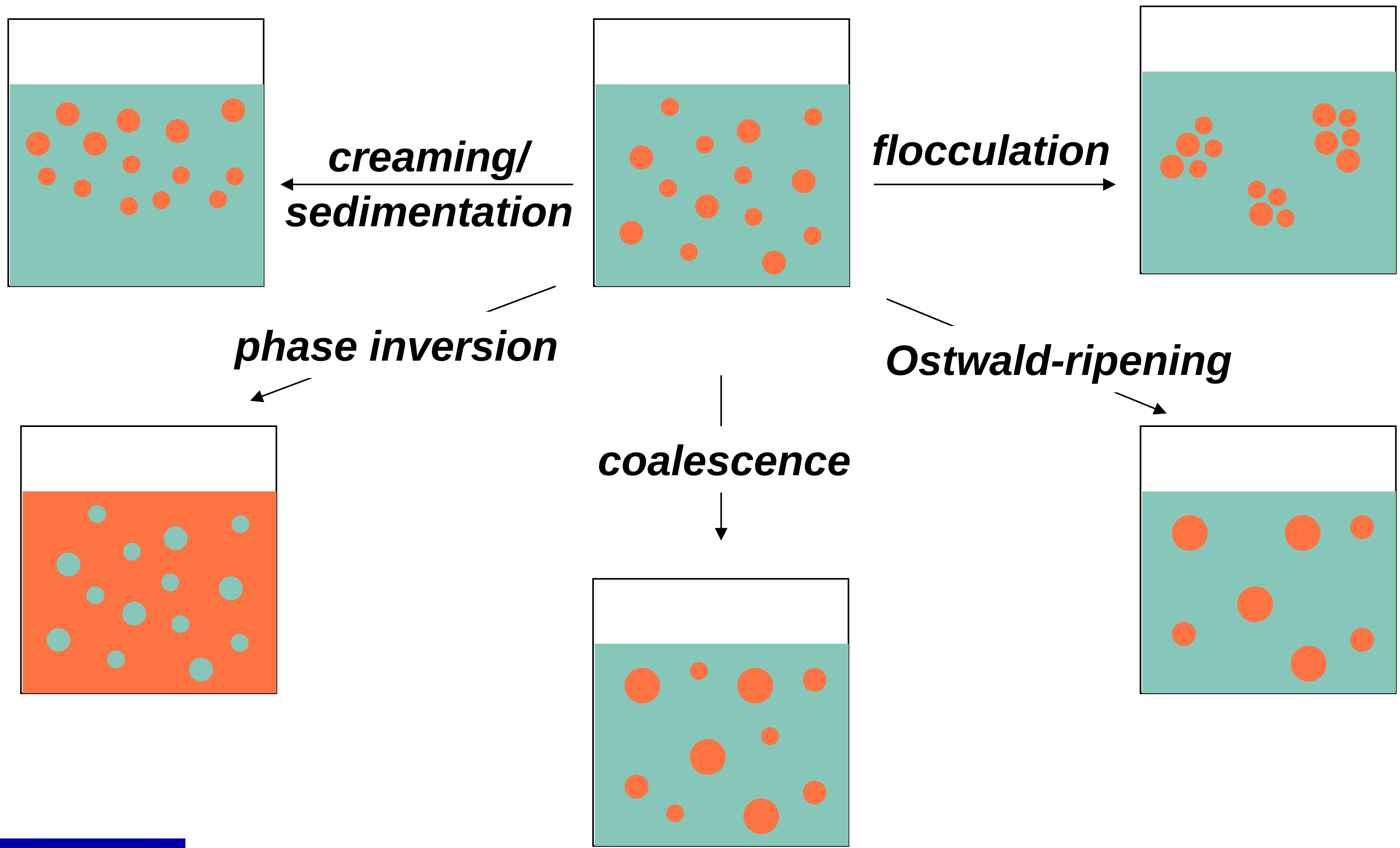
Liquid-Liquid Dispersion Phenomena

Process objectives vary according to desired product but include:

- Nature of the dispersion: O/W, W/O, O/W/O, W/O/W
- Drop size and distribution of resulting dispersion
- Kinetics of the dispersion: time scale to reach equilibrium or required DSD
- Stability of the dispersion: tendency to resist
  - coalescence; rate of coalescence
  - creaming
  - flocculation

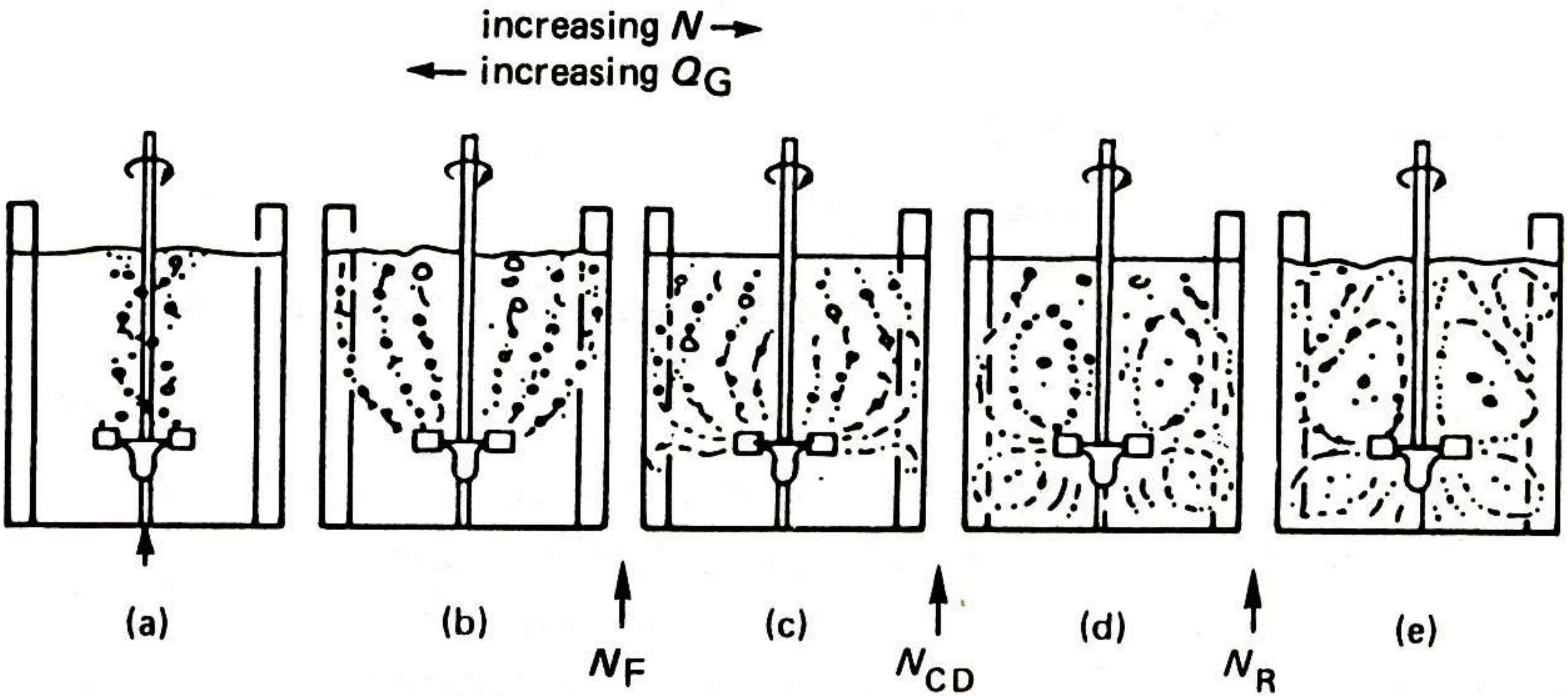
Liquid-Liquid Dispersion Phenomena

Mechanisms causing physical instability



GAS-LIQUID MIXING

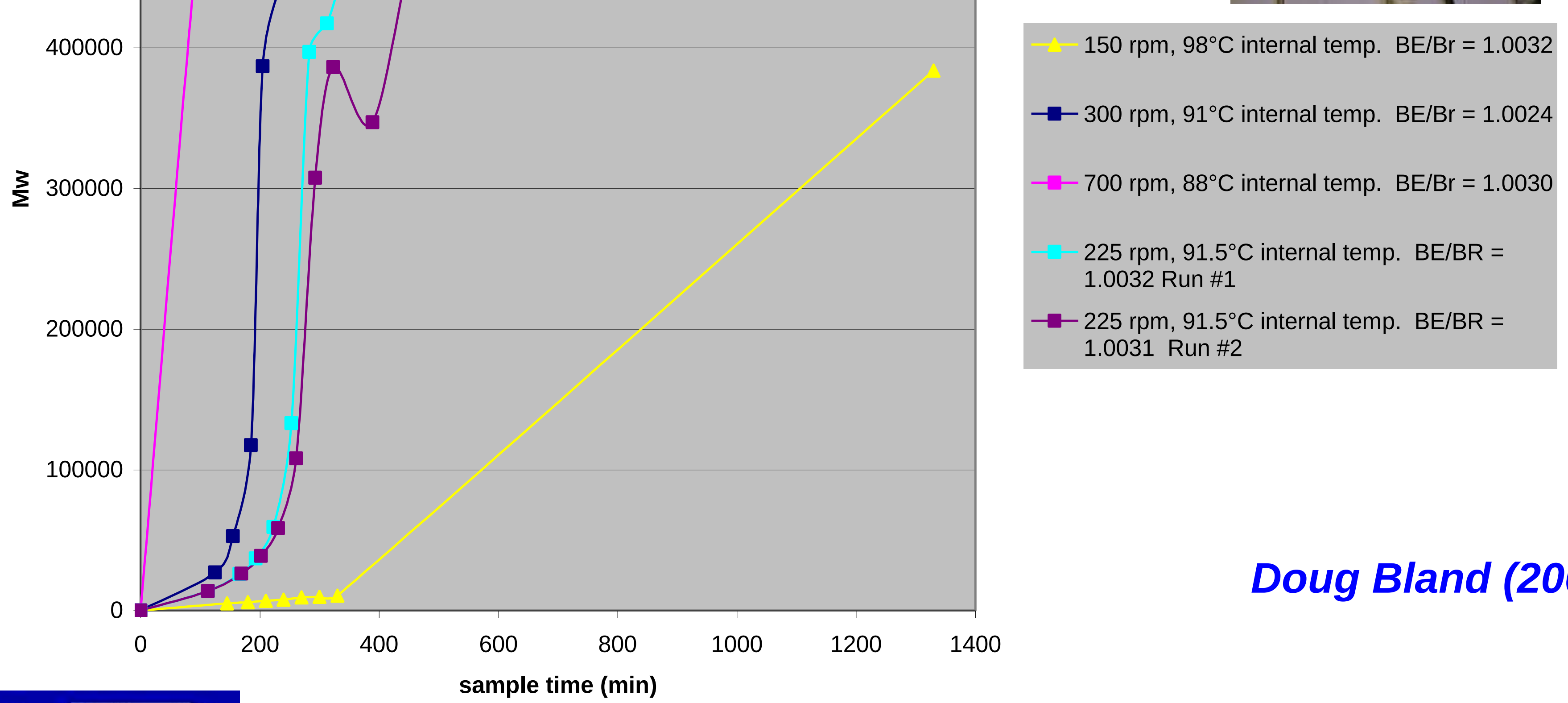
States of gas dispersion



Flooding | **Loading** | **Complete dispersion**

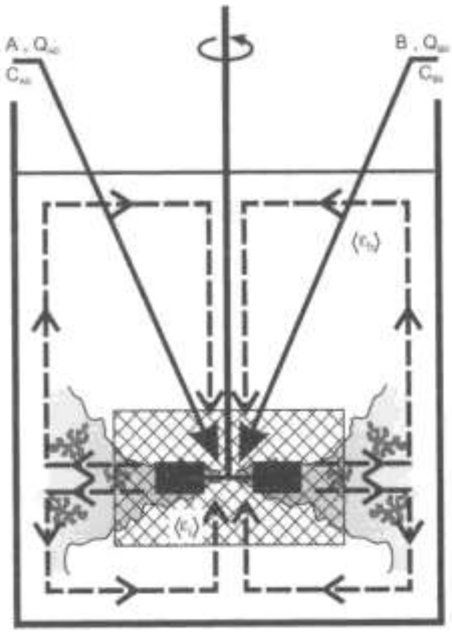
Increasing impeller rotational speed, N

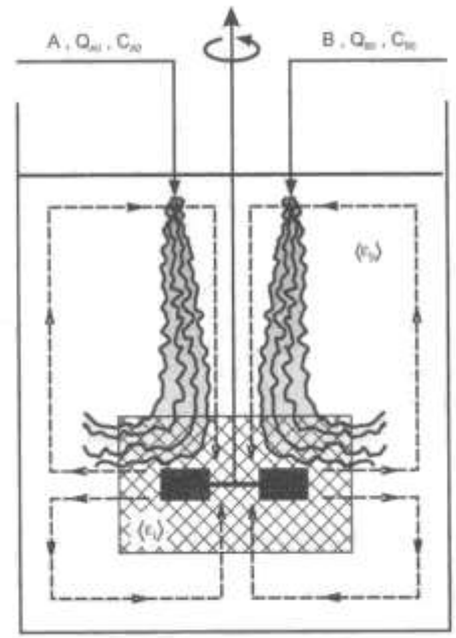
Polymerization reaction: Effect of impeller speed

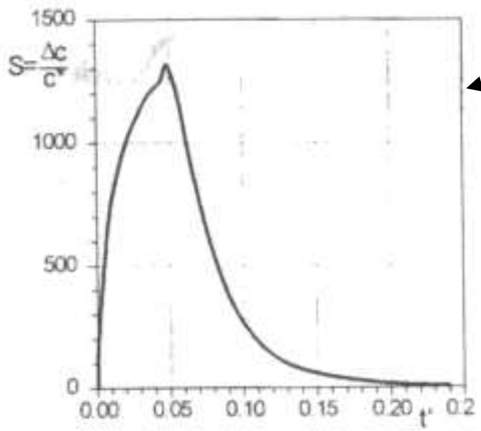


Doug Bland (2004)

Precipitation reaction: Effect of feed location

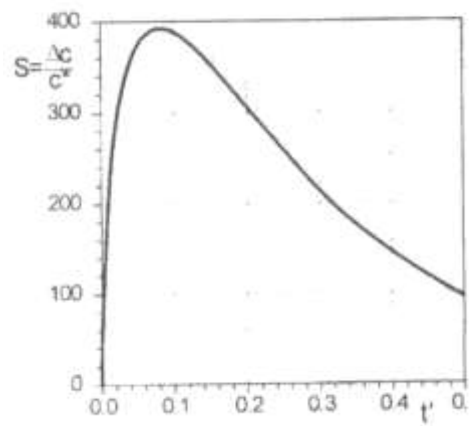






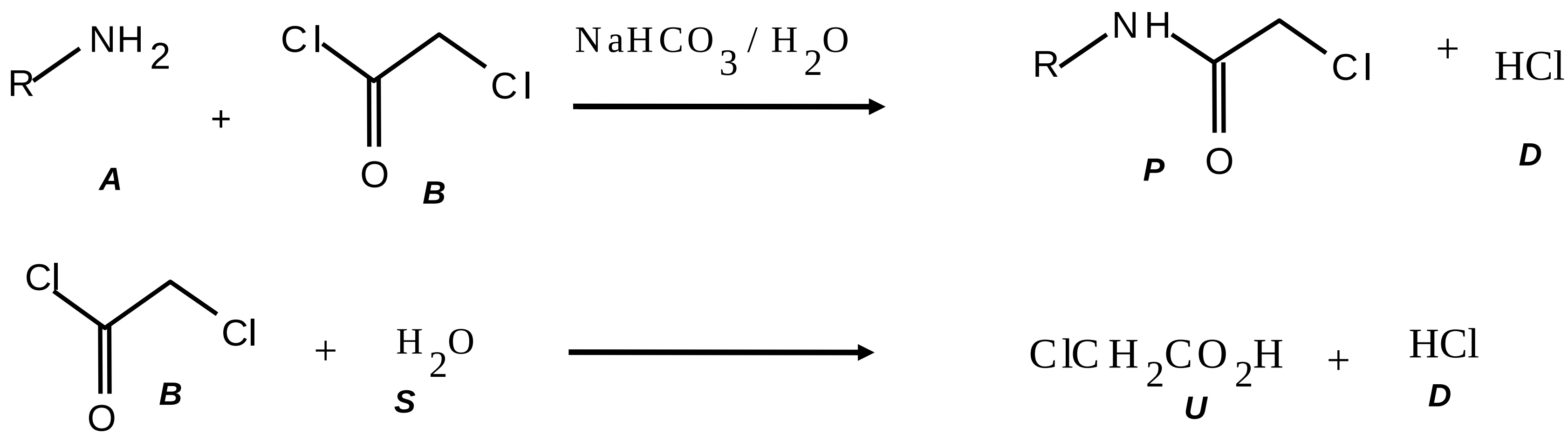
Supersaturation profiles

- Sharpe S profile ➔ many small crystals and non-uniform crystal size distribution
- Broader S ➔ larger and more uniform crystals



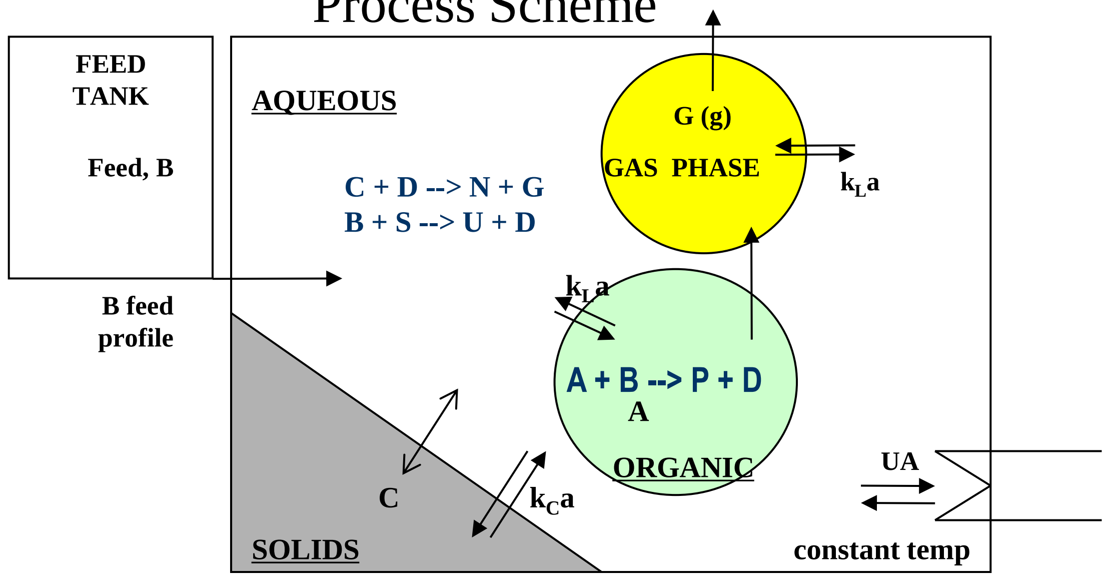
Baldyga et al (1995) CES 50(8)

Multiphase Reactions - Chloroacetylation Reaction: Effect of mixing



$$\underset{D}{HCl} + \underset{C}{NaHCO_3} \longrightarrow \underset{N}{NaCl} + \underset{G}{CO_2} + \underset{S}{H_2O}$$

Process Scheme

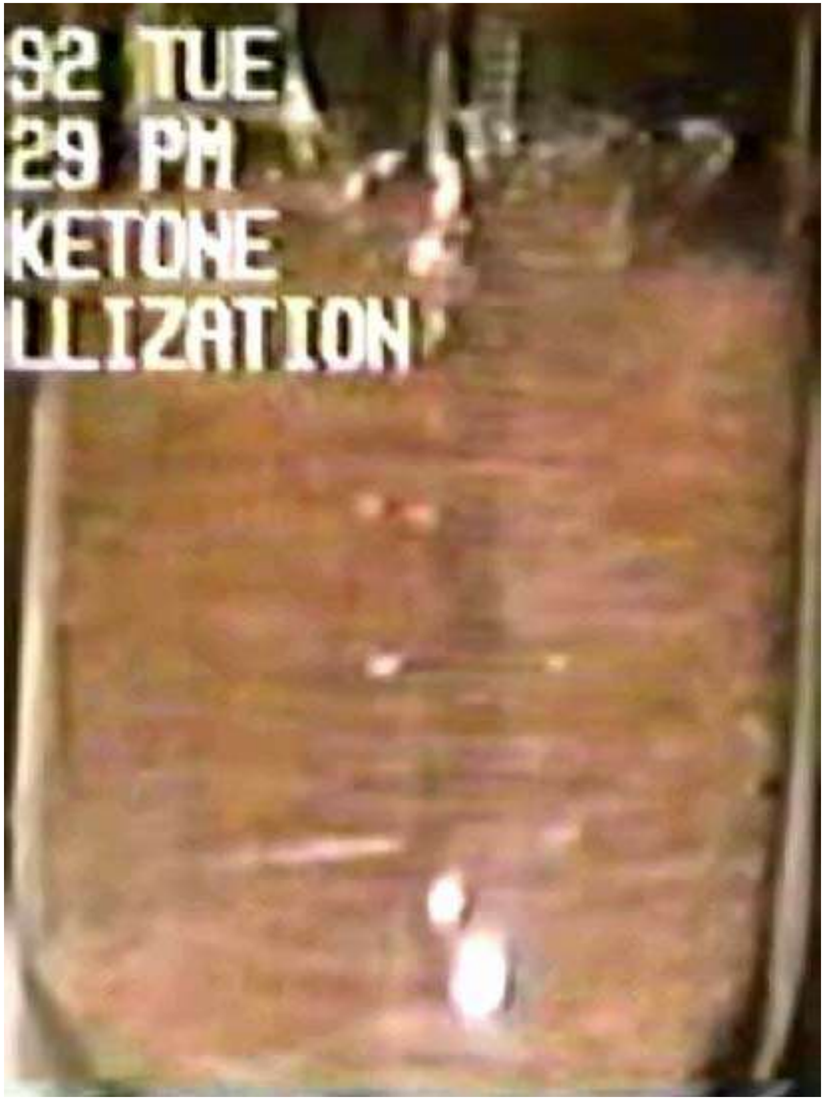


Multiphase Reactions - Chloroacetylation Reaction: Effect of mixing

Mixing Option	RPM	Feed Time	pH	Yield
2 PBT	300	3.7 hours	3.2	70%
2 PBT	400	3.5 hours	4.5	87%
2 PBT	400	5.7 hours	6.1	**~90%**

Mixing Option	RPM	Feed Time	pH	Yield
3 PBT	300	3.5 hours	5.3	87%
3 PBT	400	3.5	6.6	91%
3 PBT	400-750	3.5	6.6	**94%**

Cooling crystallization: Effect of nucleation temperature



Desired Process Result

- High crystal yield in reasonable batch time
- Prevent encrustation on vessel wall

Solution

Induce nucleation near 30° C

Summary

Focus on achieving desired process result

- *Link "effective mixing" to* ***achieving desired process result***

Describe effective mixing in terms of

- ***required hydrodynamics and relevant physicochemical phenomena necessary for process success***
- ***confirm with basic calculations, experiments and/or modeling***

Recommend/select equipment and/or operating conditions *to achieve desired process result*

Ascertain reliability of mechanical design

Closing remarks

- Mixing is usually not taught, not usually appreciated
- Mixing is key to success of many industrial processes
- Early assessment of mixing impact is crucial
- Knowledge of CFD is not equivalent to knowledge of mixing
- Improve industrial awareness of importance of mixing
- Courses in-house or otherwise
- Encourage and engage in thought experiments
- Observe live experiments
- Address industrial mixing challenges/opportunities
- **Develop next generation of experts**

Resources & Tools

http://www.1.mixing.net/

Fluid Mixing Processes (FMP)
An Industrial Consortium

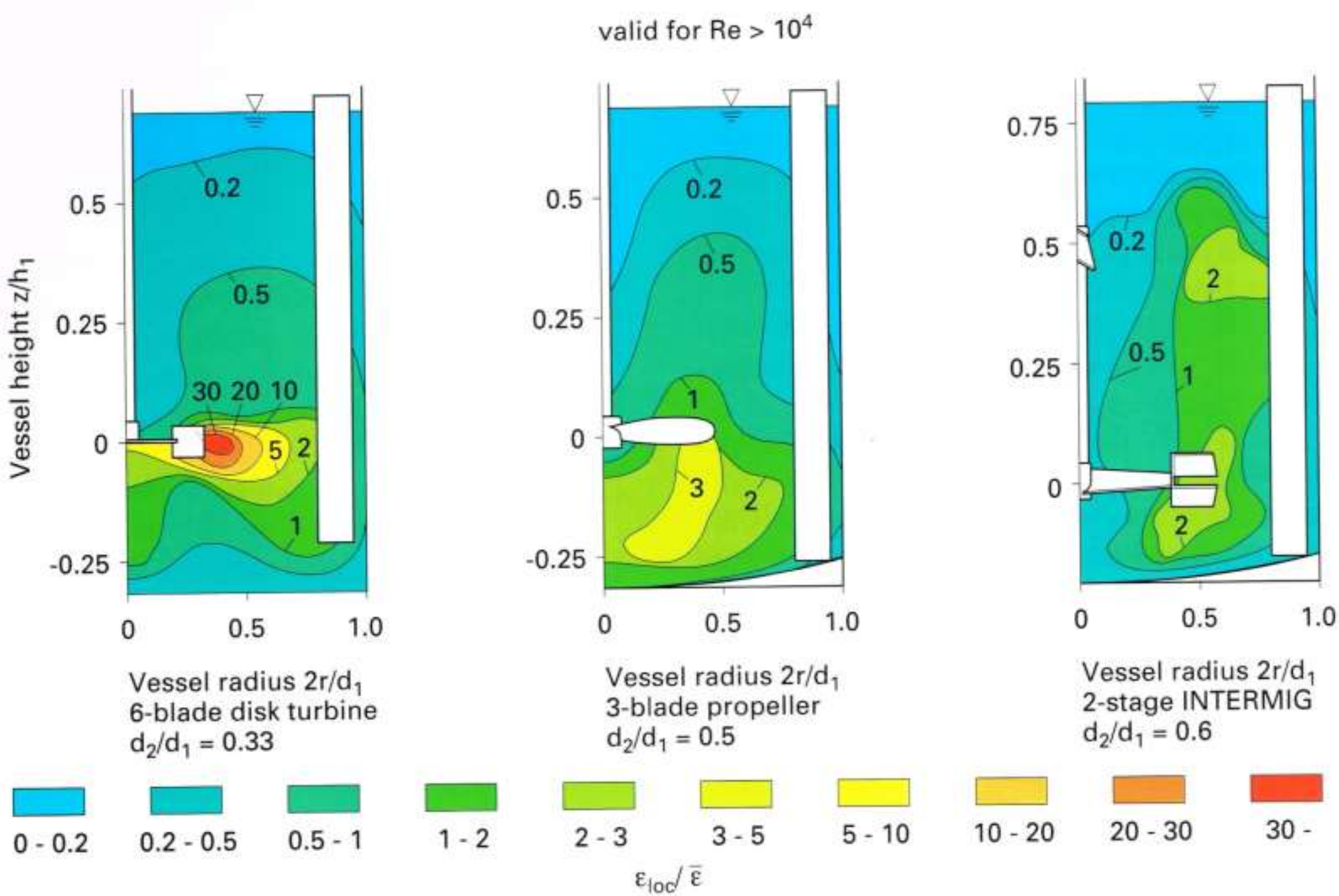
TURBULENT® 2Kx
Low viscosity liquids and multi-phase systems

LAMINAR® 2Kx
Highly viscous and non-Newtonian media

http://www.visimix.com/

Thank You!

Distribution of turbulent kinetic energy in stirred tank

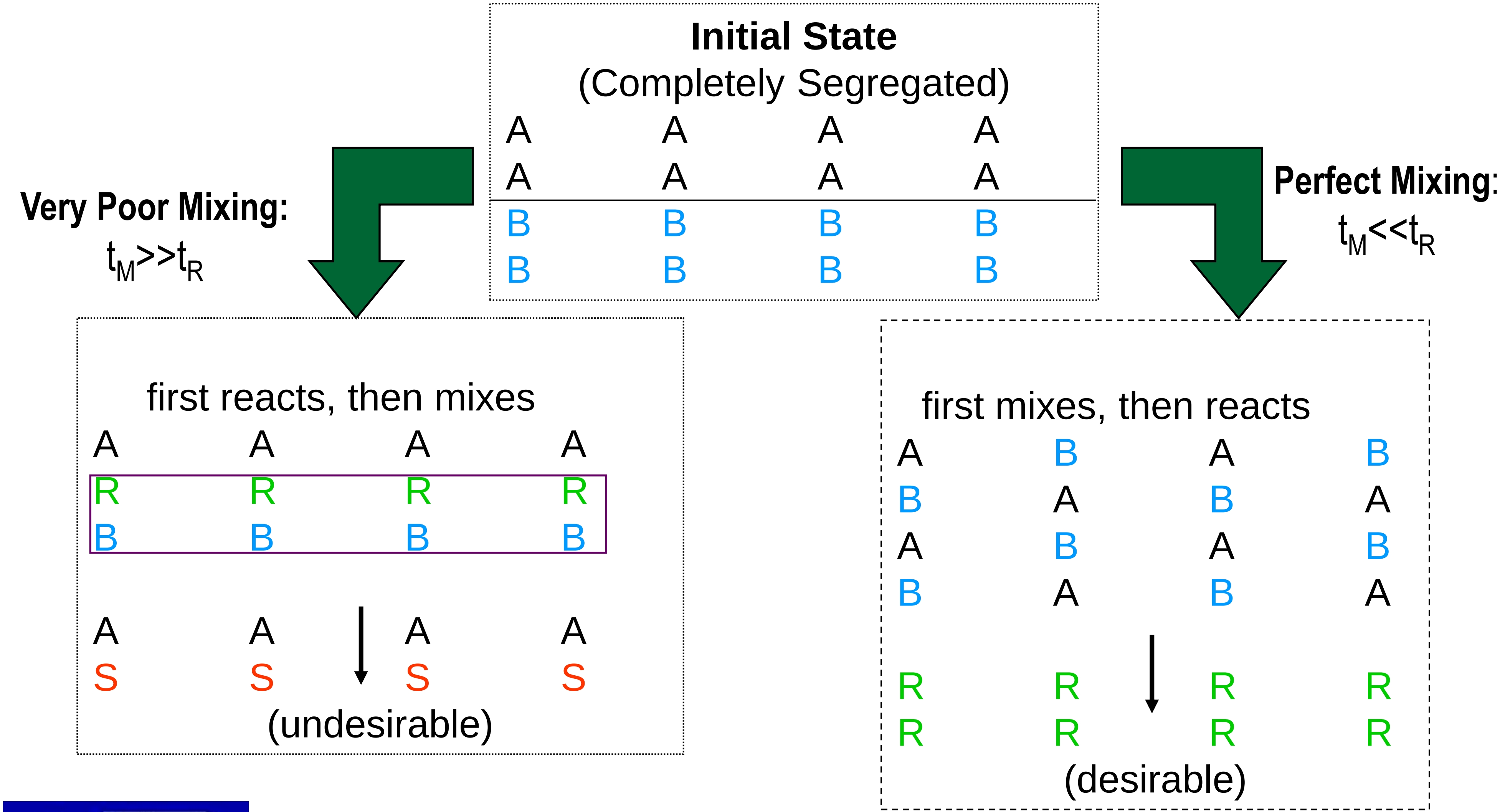


From Ekato Handbook of Mixing Technology (2000)

Effect of mixing on reactions

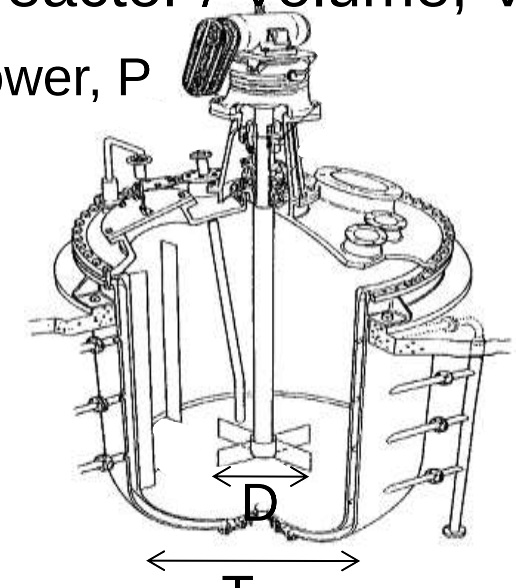
A+B→R (desired reaction)

R+B→S (undesired reaction)



Heat Transfer in jacketed agitated vessels

Agitated jacketed reactor / Volume, V



$$q = h_{process} A \Delta t$$

$$h_{process} = C \left(\frac{P}{V} \right)^{2/9} \left(\frac{D}{T} \right)^{2/9} T^{-1/9}$$

$$C = f\left(physical\ properties \right)$$

- ***$h_{process}$* -very weak effect of specific P/V**
- ***P/V must increase by factor of 23 to double $h_{process}$!***

Adding heat transfer area is more effective!