The Role of Mixing in Fast, Competitive Chemical Reactions

Richard Grenville
Director of Mixing Technology

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FOR PDF OF PRESENTATION…….

rkgrenville@philamixers.com

AGENDA

Is mixing important?

CSTR design and operation:

- Assumption of “perfect back mixing”
- By-passing

Chemical reactions:

- Simple vs. competitive
- Mixing issues and reduction of yield on scale-up

Timescales of mixing and reaction:

- Damkohler number

Agitator design for fast, competitive chemical reactions

Examples

Conclusions

IMPORTANCE OF MIXING

Smith, ChERD., 1990:

- US chemical industry loses \$ 10^{10} each year due to poor mixing:
  - 1 % increase in yield → ~ \$ 10^6
  - One day of down time → ~ \$ 10^6

Examples:

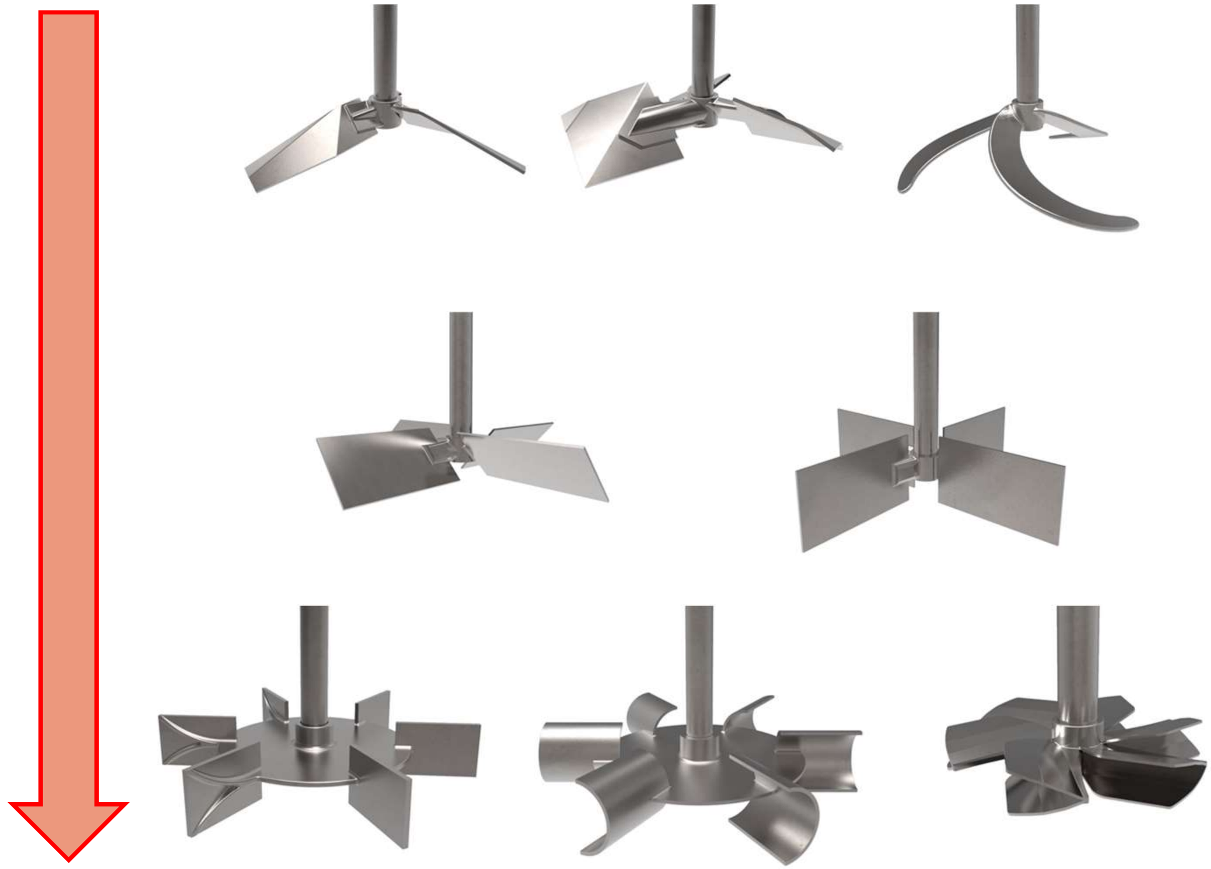
- Lower than expected yields in chemical reactions
- Longer than expected batch / cycle times
- Stagnation, fouling and build-up of solids
- Solids settled on base of vessel
- Poor mass transfer – any multiphase system
- Poor heat transfer
- Others……………..?

IMPELLER TYPES

Hydrofoils
“Low shear”
“High efficiency”

Pitched and flat blade turbines
“Mixed flow”

Disc turbines
“High shear”
“Low efficiency”



Increasing “shear” (Ducoste et al., AIChEJ, 1997)

PROCESS RESULT

Mix components to promote chemical reaction:

- Semi-batch and continuous

Minimize side reactions:

- Formation of by-products
- Waste of raw materials
- Increased separation and disposal costs

Minimize scale-up issues:

- Change in yield on scale-up:
  - Including molecular weight distribution (polymerization); particle size distribution and crystal polymorph (crystallization or precipitation); etc.

PERFECTLY MIXED REACTOR

"The CSTR is normally run at steady state, and is usually operated so as to be *quite well mixed*", (Fogler, Elements of Chemical Reaction Engineering 2nd Ed., 1992)

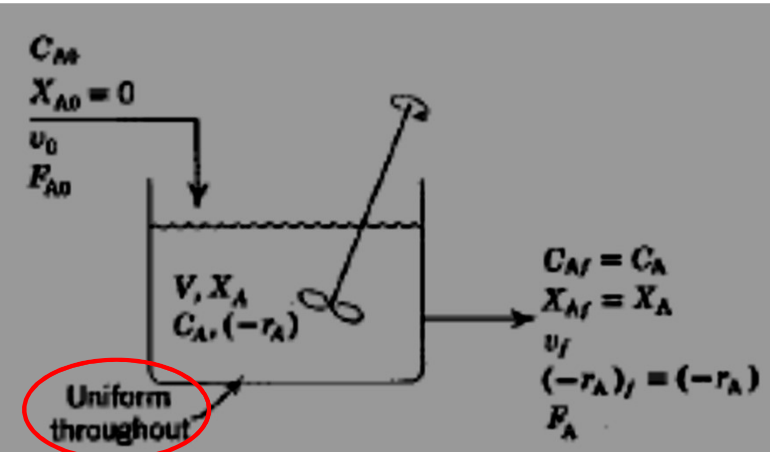


FIGURE 3. Notation for a mixed reactor.

From Levenspiel, "Chemical Reaction Engineering. 2nd Ed., 1972

Assume that exit composition is same as reactor contents

IDEAL CSTR

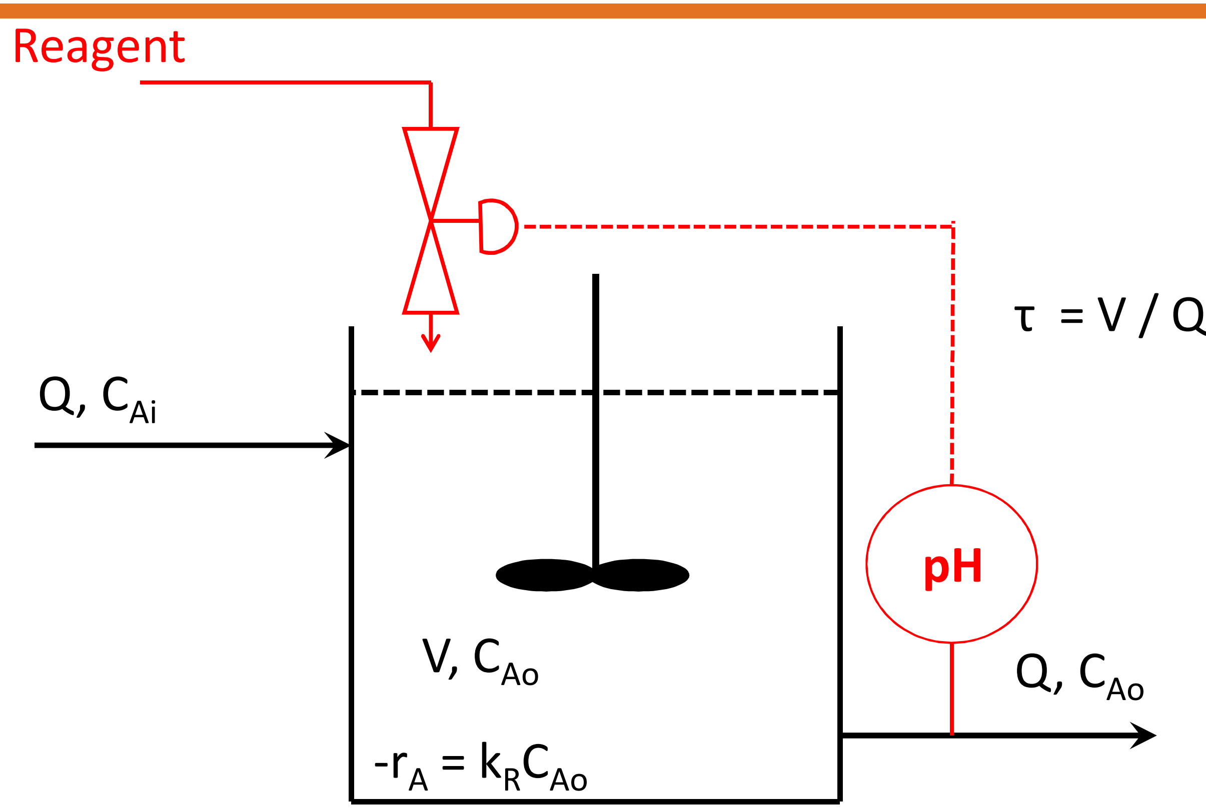
If vessel is perfectly back mixed composition of fluid leaving vessel is <u>equal to composition in the vessel</u>

Assumption made in the design of systems for pH control in WWT

Rule-of-thumb, vessel is back mixed if:

$\tau = \Omega\,\theta$

$5 < \Omega < 10$



$$C_{Ao} = \frac{C_{Ai}}{(1 + k_R \tau)}$$

$$X = 1 - \frac{1}{(1 + k_R \tau)}$$

RTD – PERFECT BACK MIXING

If vessel is "perfectly back mixed" residence time distribution (RTD) can be analytically calculated

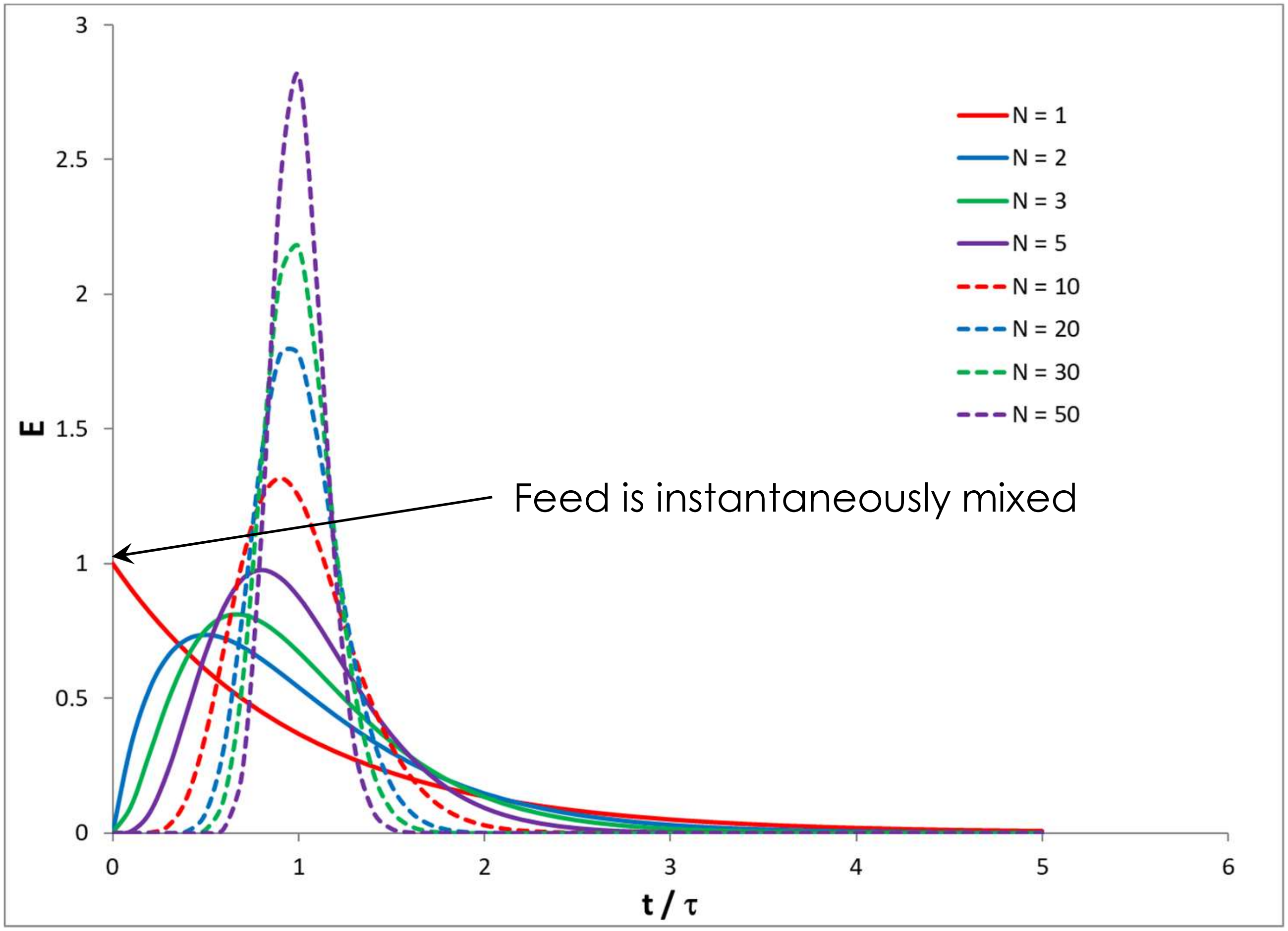
Can be combined with reaction kinetics to estimate conversion

Increasing number of tanks-in-series approximates plug flow

Slow reaction rates – compared to mixing rates

Vessel contents are homogeneous in space and time

When does assumption fail?



CSTR – RTD & BY-PASSING

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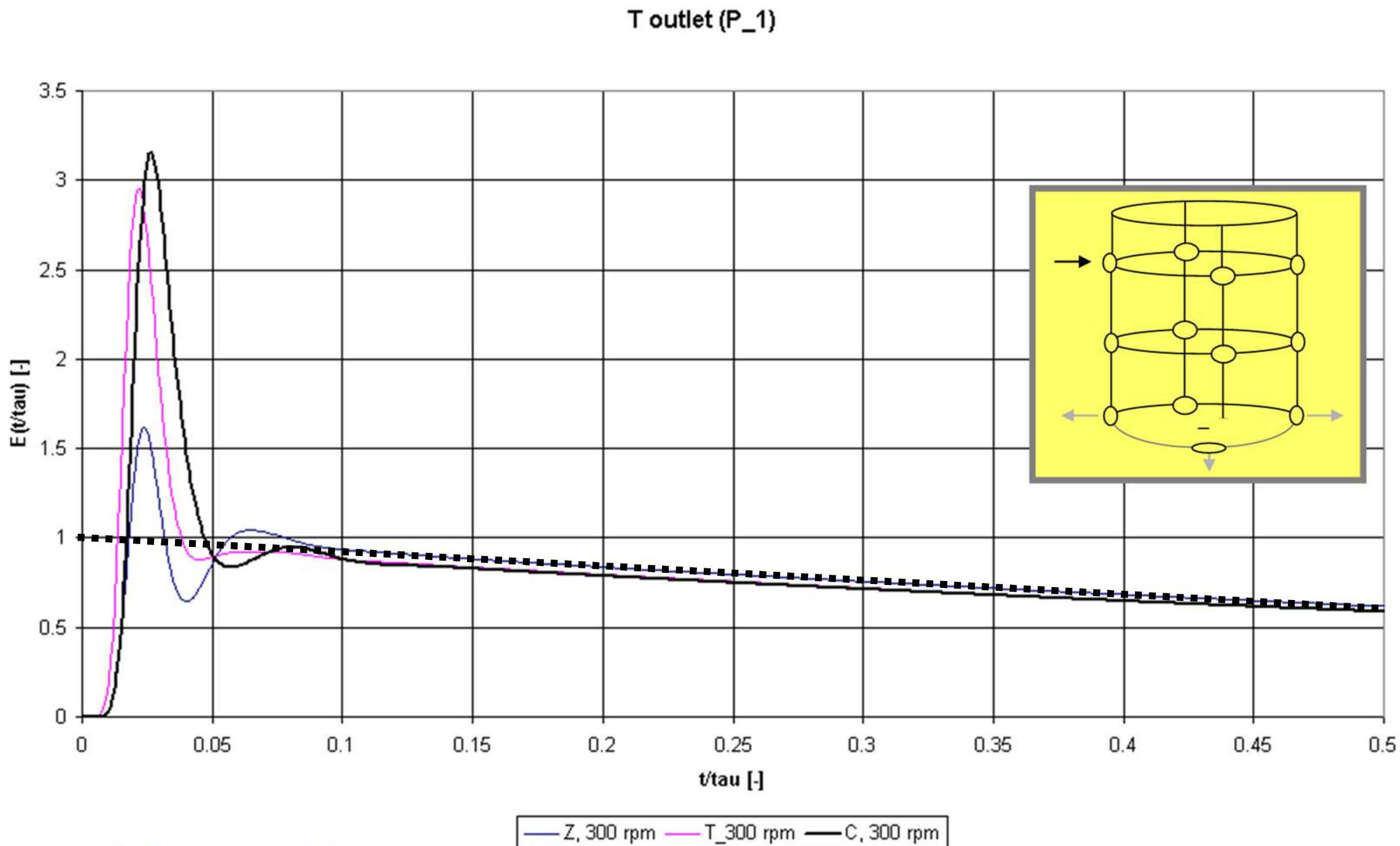
Some material leaves early –compared to prediction of "perfect back mixing"

Therefore that material is under-converted

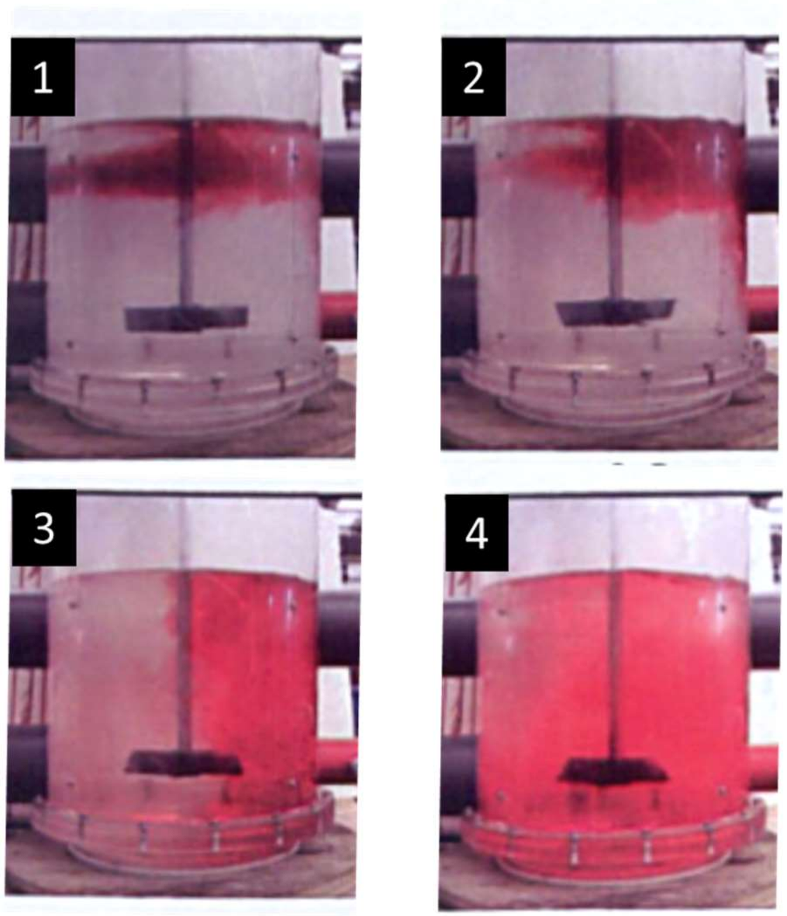
Spent less time than expected in reactor

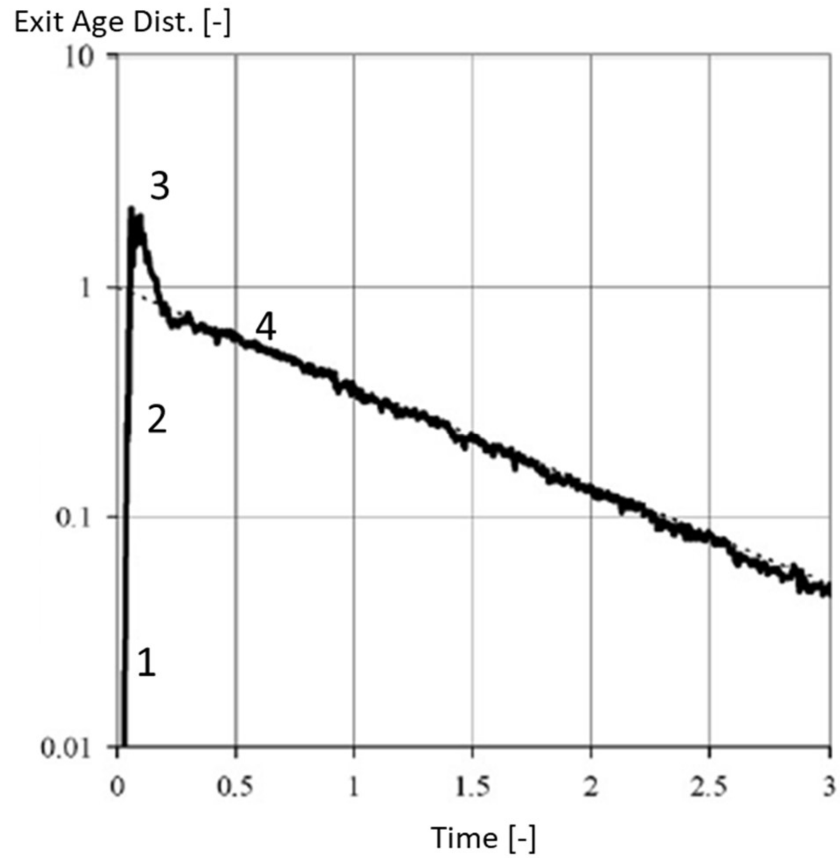
Need to eliminate by-passing



Jones, *PhD Thesis*, KCL, 2004

BY-PASSING





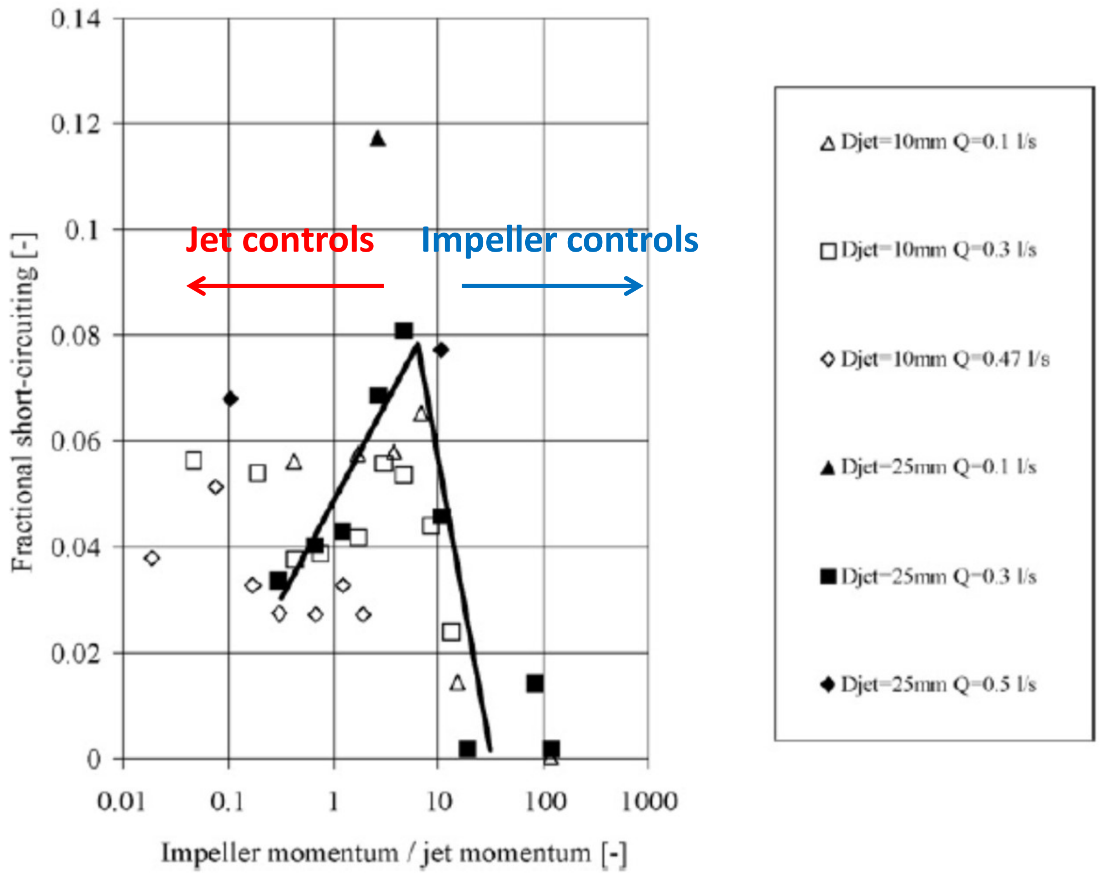
Jones et al., ChERD., 2009

MOMENTUM RATIO

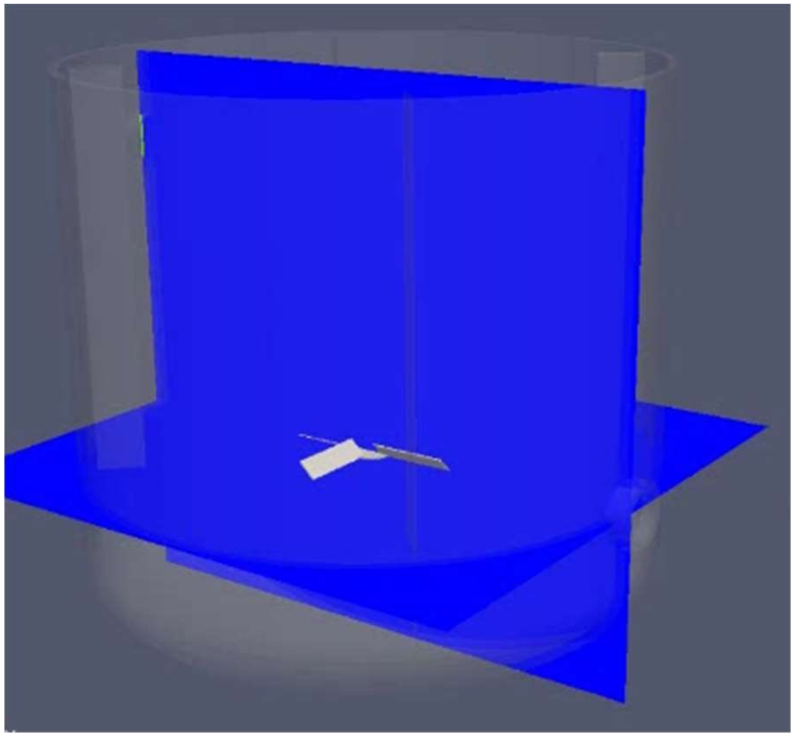
Need flow generated by impeller to control flow patterns in vessel

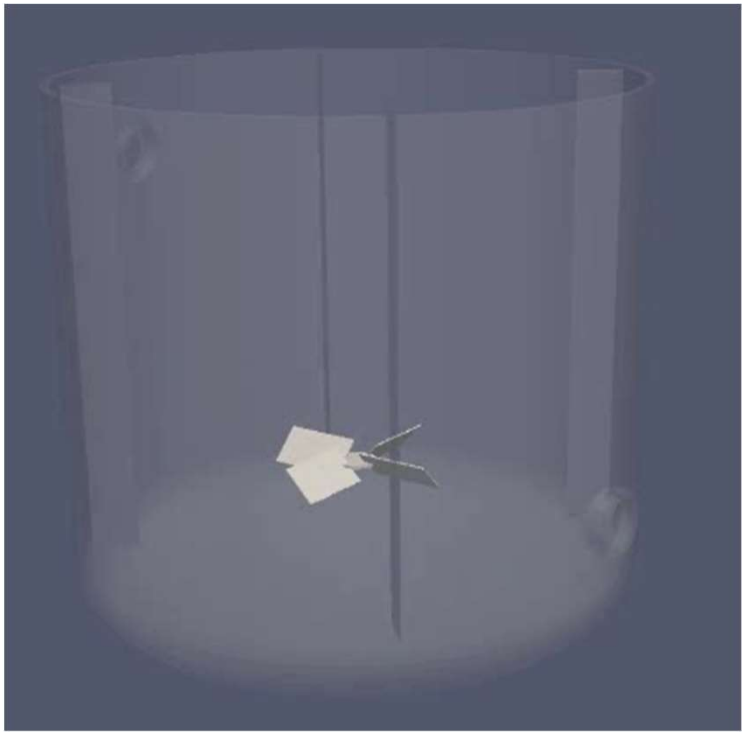
Ratio of impeller flow momentum to feed jet momentum determines operating regime

Also need to consider location and direction of feed



CFD MODELLING





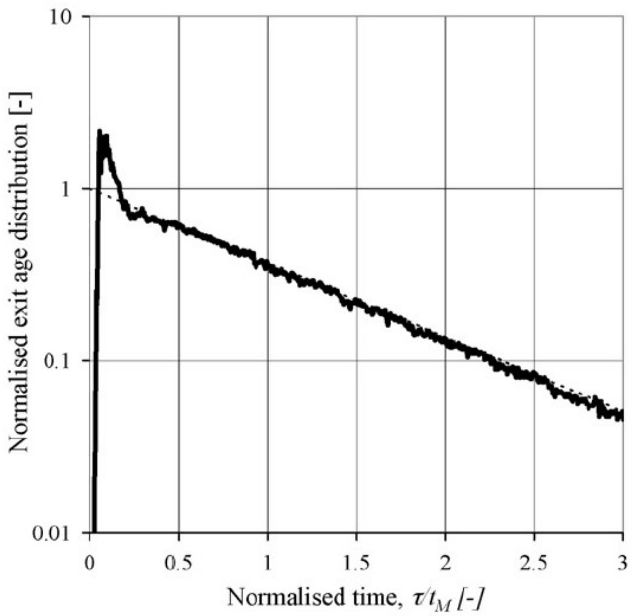
Modelling case from Jones et al: $D_{PBT} = 0.1$ m, $D_{jet} = 0.025$ m, $Q = 0.3$ l/s, $N = 1\ s^{-1}$

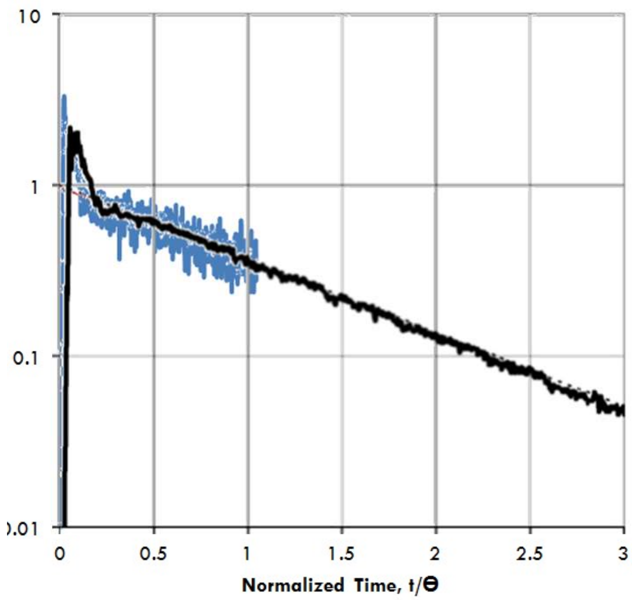
Thomas et al., AIChE Meeting, 2015

Runtime: 10 hours on 160 cores

EXPERIMENT & MODEL

Exit Age Dist.





Jones et al., 2009

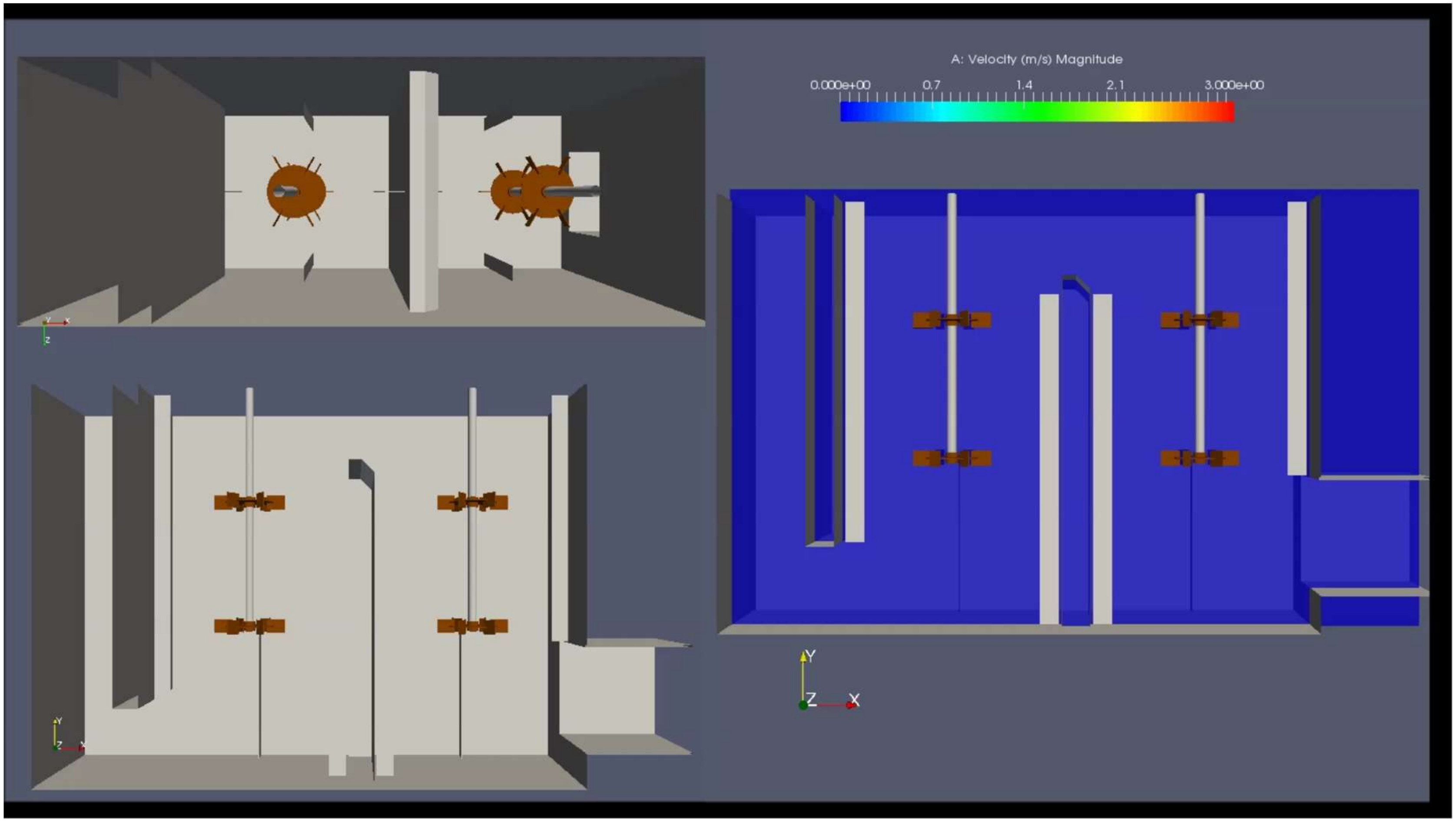
Measured ϴ: 68.9 s

LES-CFD Prediction

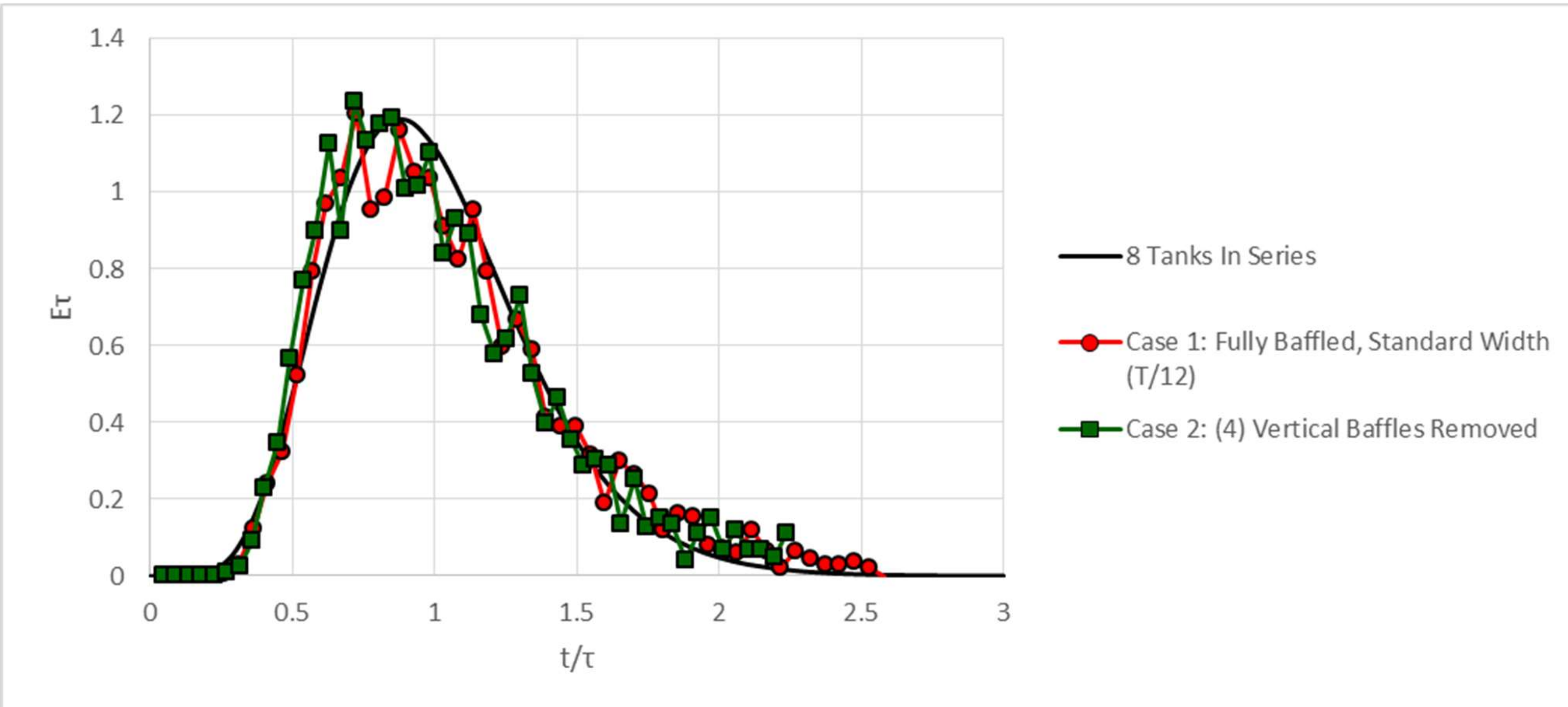
Predicted ϴ: 68.5 s

No need to run model for ~5x τ

WATER TREATMENT RAPID MIX TANK



RTDs - ~8 TANKS IN SERIES



TYPES OF REACTION

Some reactions are fast ("instantaneous") and some reactions are competitive

Simple, non-competitive reaction:

$$A + B \rightarrow C + D$$

A = HCl   B = NaOH   C = NaCl   D = H_2O

The Rate of Mixing has no influence on the outcome of the reaction

TYPES OF REACTION

Many (valuable) reactions are competitive:

$$A + B \rightarrow C$$

$$B + C \rightarrow D$$

$A = CH_3C_6H_5$ $B = NO_2^+$ $C = CH_3C_6H_4NO_2$ $D = CH_3C_6H_3(NO_2)_2$

Example:

- Want to make mononitro-toluene
- Dinitro-toluene is a possible by-product
- So is trinitro-toluene

ASSUMPTION OF PERFECT MIXING

Timescale of the reaction must be longer than Blend Time:

- Assumption of perfect mixing is valid
- Outcome of reaction is determined by kinetics

In a turbulent stirred tank, the blend time is generally in the order to 10's of seconds

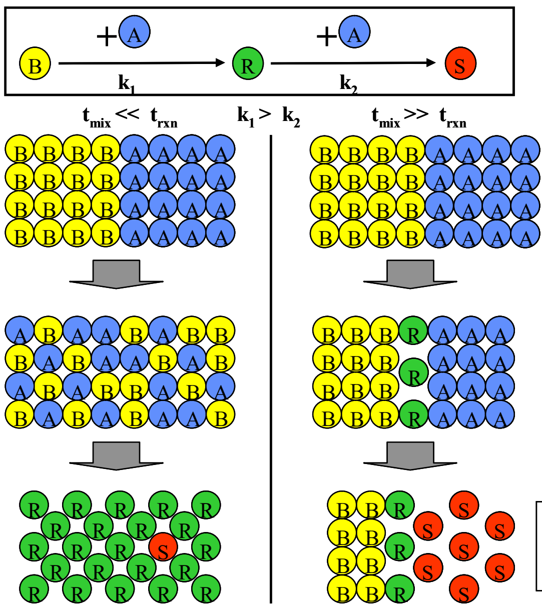
If Half-Life of Reaction is greater than ~60 seconds, then reactor is perfectly mixed (as far as reactants are concerned)

So what is the problem …..?

MIXING ON MICRO-SCALE

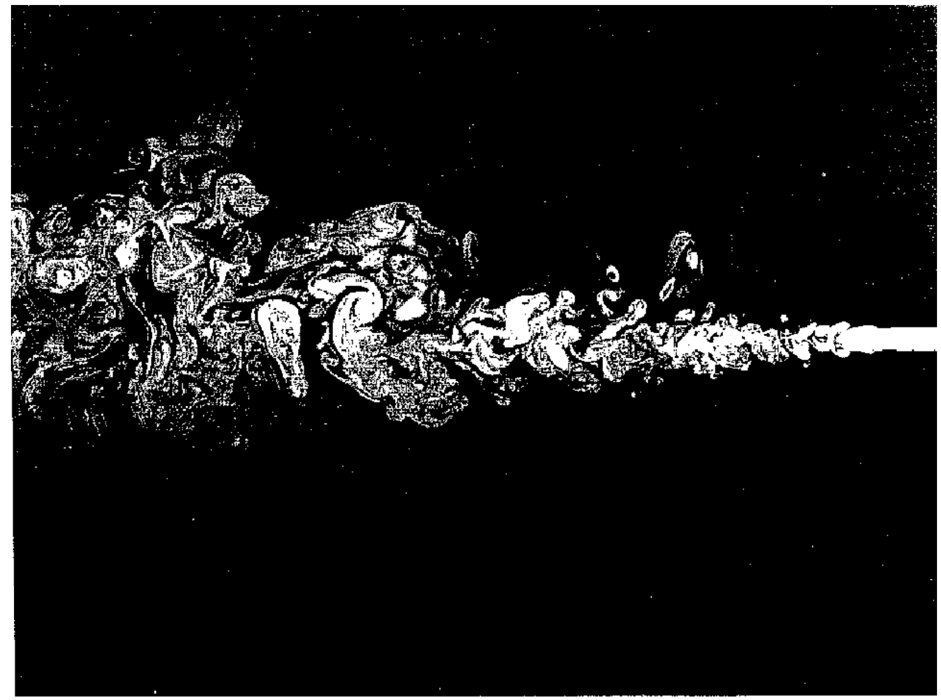
Mixing sensitivity of competitive-consecutive fast reaction scheme

- schematic representation



Kinetics limit, slow reaction regime, $X_S \to 0$

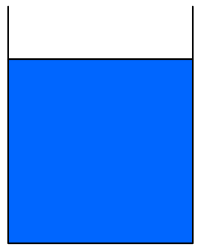
Mixing limits, instantaneous reaction regime, $X_S \to 1$



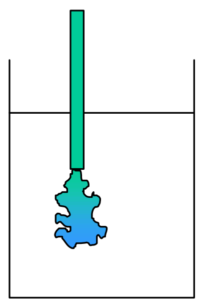
Mixing sensitivity from Hannon *et al.*, MIXING XVII, 1999

Scales of mixing from Dimotakis *et al.*, Proc. XV Int Symp Fluid Dyn, 1981

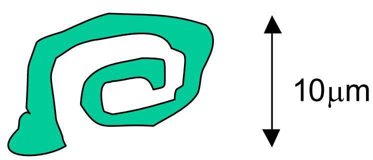
TIMESCALES OF MIXING



Macro-mixing:
- scale of the tank
- blend time



Meso-mixing:
- scale of the feed zone
- dispersion of feed plume



Micro-mixing:
- smallest scales of turbulence
- diffusion time

MIXING TIMESCALES

Macromixing → at scale of the vessel:

- Time for vessel contents to become homogeneous
- Blend time

Micromixing → at scale of smallest turbulent eddies:

- Deformation of fluid elements (vortex stretching, engulfment)
- Diffusion

Mesomixing → at scale of feed plume:

- Turbulent exchange of fresh feed with surrounding fluid
- Erosive reduction in scale of “blobs” of feed

Baldyga & Pohorecki, Chem. Eng. J., 1995

MESO-MIXING

Meso-mixing Time (Bourne *et al.*):

- Semi-batch or continuous reactor - adding B to A
- Time for "plume" of B to be dispersed in A by local turbulence

More complicated than micro-mixing:

- Time is dependent on local mixing conditions <u>and</u> feed rate of B

$$t_M = 2\left(\frac{L_C^2}{\varepsilon}\right)^{1/3} = 2\left(\frac{q_B}{\overline{U}\varepsilon}\right)^{1/3}$$

Local energy dissipation rate and mean velocity at feed location

REACTION TIMESCALE

Reaction Time is determined by:

- Rate constant.
- Concentration(s).

In a perfectly mixed environment: $$t_R = \frac{1}{r_R} = \frac{1}{k_R C(A) C(B)}$$

In a poorly mixed environment: $$t_R = \frac{1}{r_R} = \frac{1}{k_R C(A) C_0(B)}$$

If mixing is too slow, reaction occurs between concentrations at the feed location where $C(B) = C_0(B)$:

- Reaction rate is faster than predicted based on "good" mixing.
- More by-product will form.

DAMKOHLER NUMBER

$$Da = \frac{r_{React}}{r_{Mix}} = \frac{t_{Mix}}{t_{React}}$$

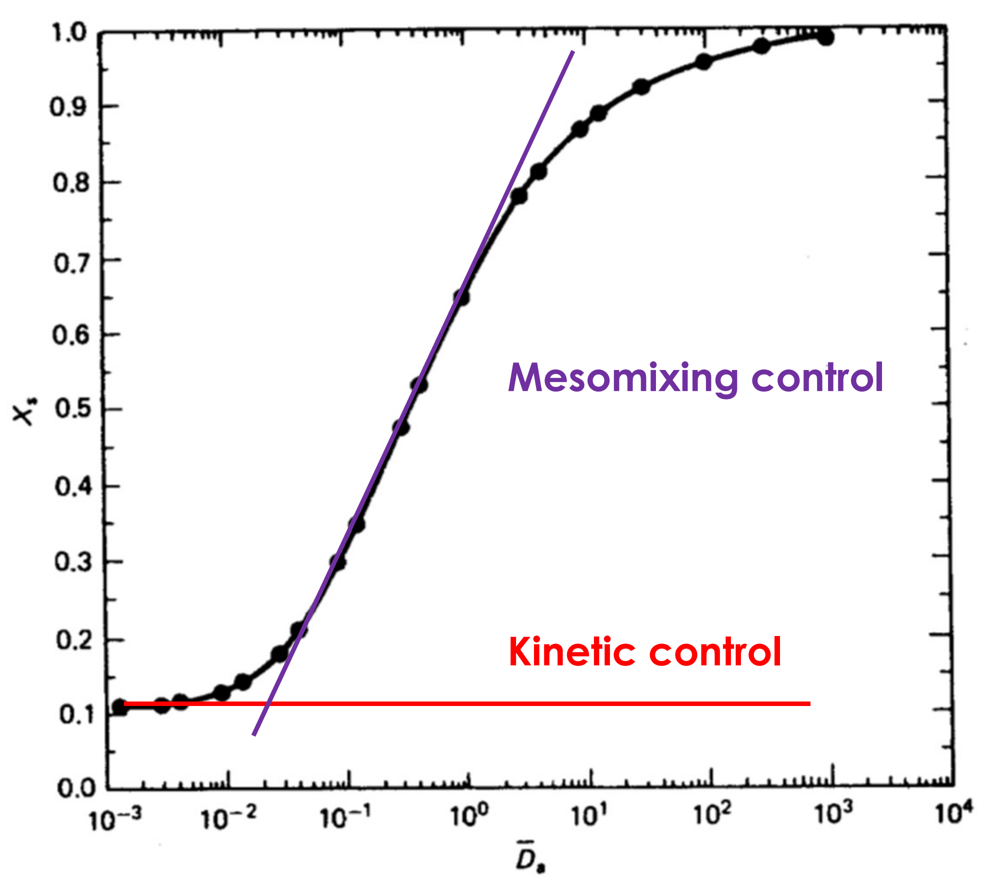
$r_{Mix} >> r_{React}$

$Da << 1$

Kinetically controlled

If chemistry (kinetics) are fixed:

$Da \propto t_{Mix}$



SCALE-UP CONSIDERATIONS

Feed location

Addition rate of B:

- Batch / feed time

Impeller type

FEED LOCATION – DIP PIPES

Feed at location of highest mixing and energy dissipation rate:

- Into the impeller zone

Effect has been well characterized and reported

Care must be taken in the mechanical design of the pipe:

- Flow induced vibration → fatigue failures

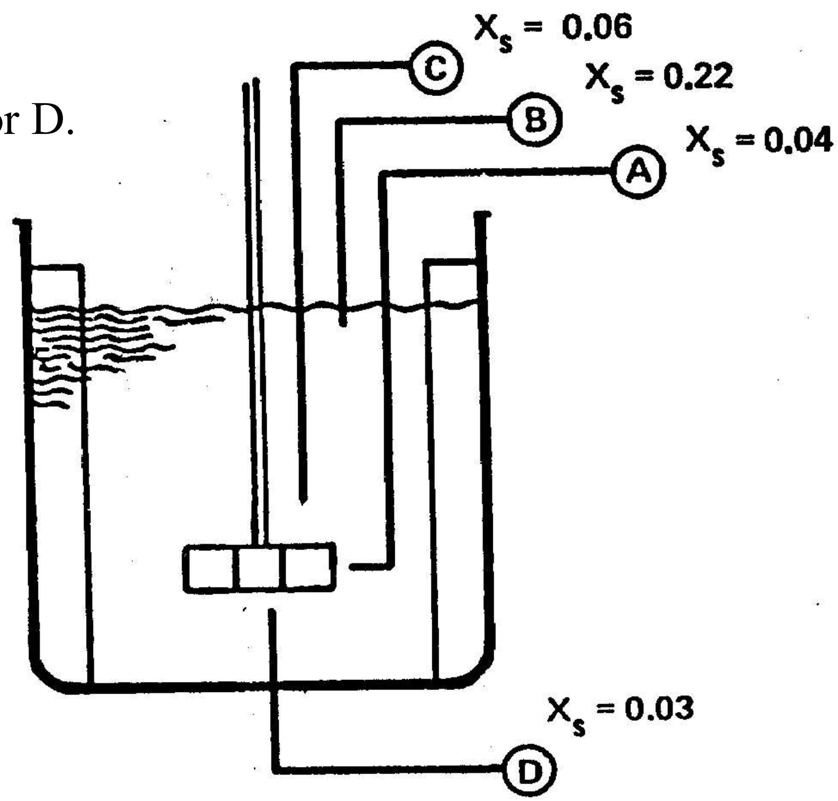
What happens if feed of B shuts off?

- Will reactor contents migrate into feed pipe?
- May have to feed above liquid surface for safety reasons

What happens if dip tube plugs?

EFFECT OF FEED LOCATION

Location B makes
6 -7 x more waste
than Locations A or D.



Tosun, 6th Europ. Conf. on Mixing, 1988

EFFECT OF FEED RATE

At low feed rates, micro-mixing controls:

- Engulfment of small-scale eddies
- Feed jet is dispersed quickly

As feed rate, q_B, increases mechanism changes:

- Dispersion of feed jet takes longer than engulfment

A critical feed time (or feed rate) can be identified:

- $t > t_{CRIT}$ Micro-mixing controls
- $t < t_{CRIT}$ Meso-mixing controls

EFFECT OF FEED RATE

Identify and operate at "knee-of-curve" (compare to Damkohler plot)

In order to operate in micro-mixing (kinetic) regime:

- Increase feed time:
  - Reduce production
- Increase agitation:
  - Power input

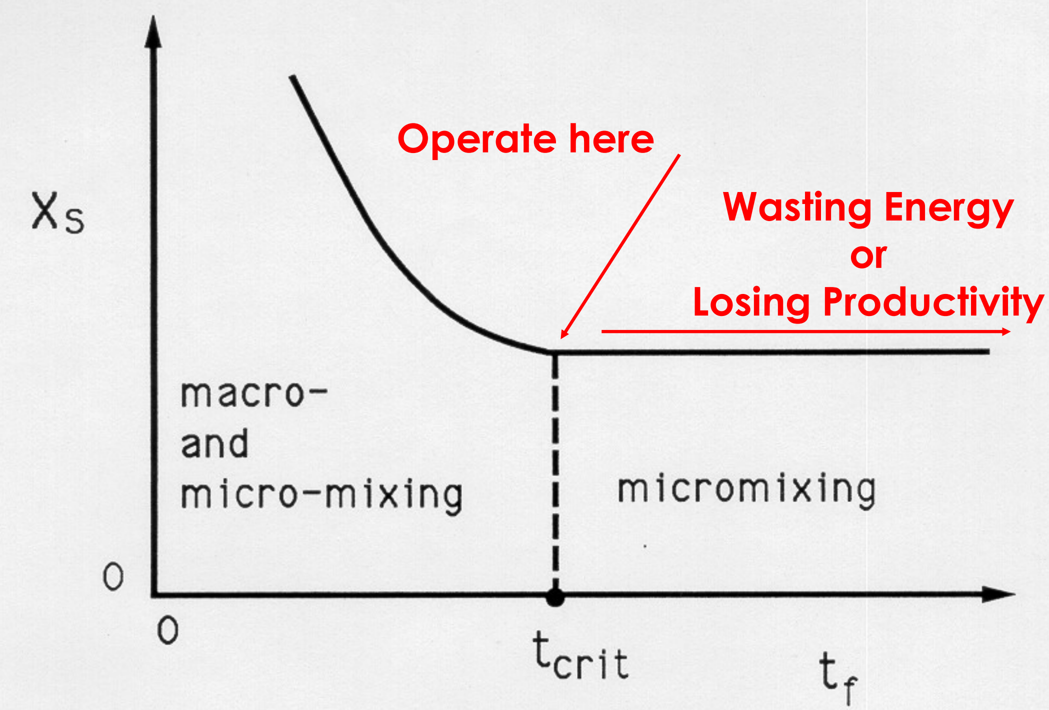


Fig. 1 Product distribution (Xs) as a function of feed time (t_f) for a semi-batch reactor

Baldyga *et al.*, Chem Eng Sci, 1993

FEED RATE

Reduce feed time – move from micro to meso-mixing control:

- Yield of desired product reduced
- Plume of B cannot be dispersed fast enough by local mixing rate

Understanding this aspect of mixing and reaction is critical to successful scale-up:

- Long feed times achievable in lab combined with high impeller speed
- Feed time in plant dictated by required production rate

“Ream-Out”:

- What if higher production rate is required (sold out)?
- Need shorter feed time

$Ca(OH)_2$ PLUME → $Mg(OH)_2$

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Feature Report

Mixing: Impeller Performance in Stirred Tanks

Characterizing mixer impellers on the basis of power, flow, shear and efficiency

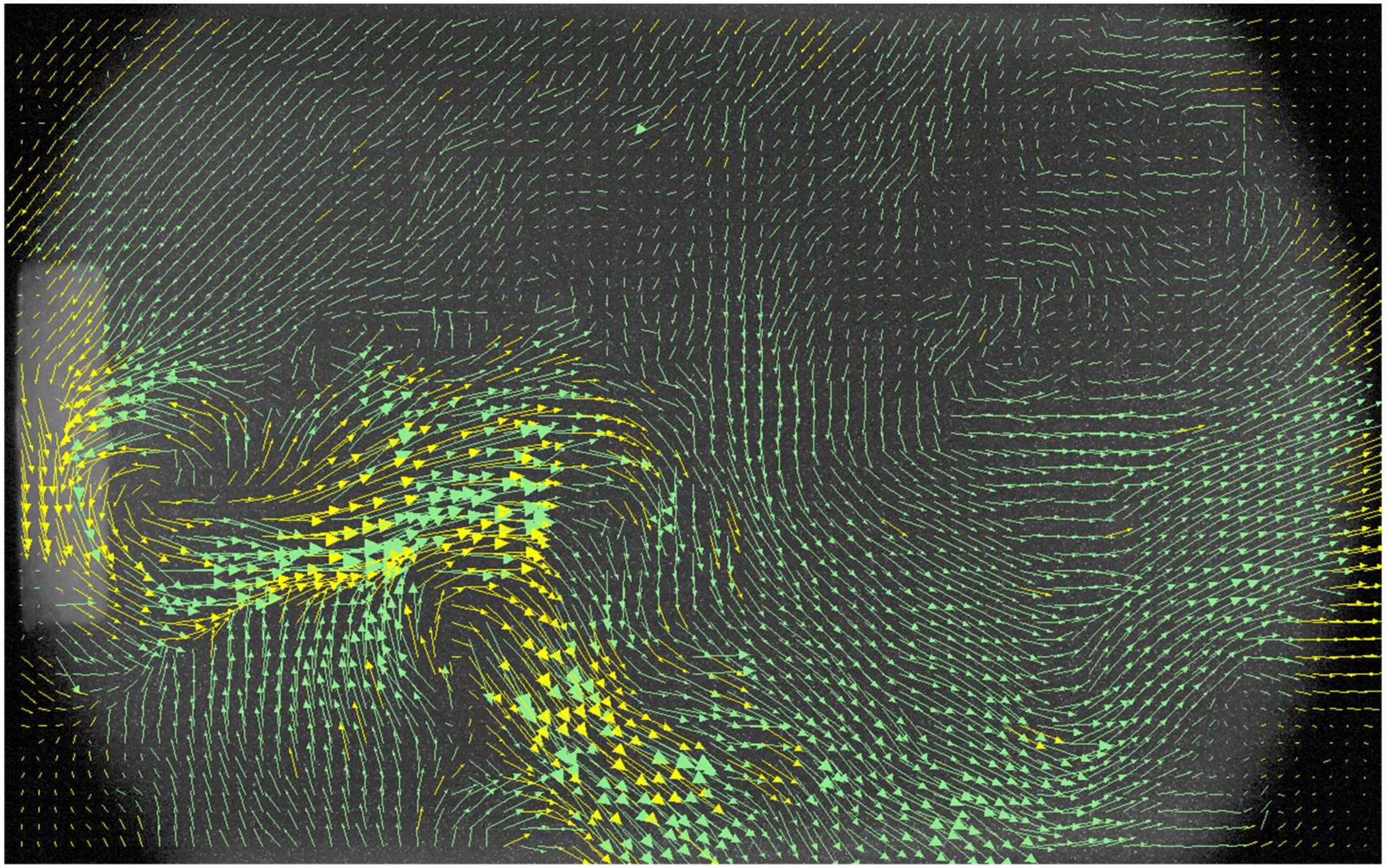
Richard K. Grenville and Jason J. Giacomelli
Philadelphia Mixing Solutions Ltd.
Gustavo Padron and David A. R. Brown
BHR Group

Mixing has been defined as "the application of mechanical motion in order to create fluid dynamic effects that achieve a desired process result" [1]. The process result is the objective of the vessel operator and will be a transformation of the ingredients fed to the vessel into a product. The goal of the equipment supplier will be to understand the role of mixing in promoting the

NOMENCLATURE

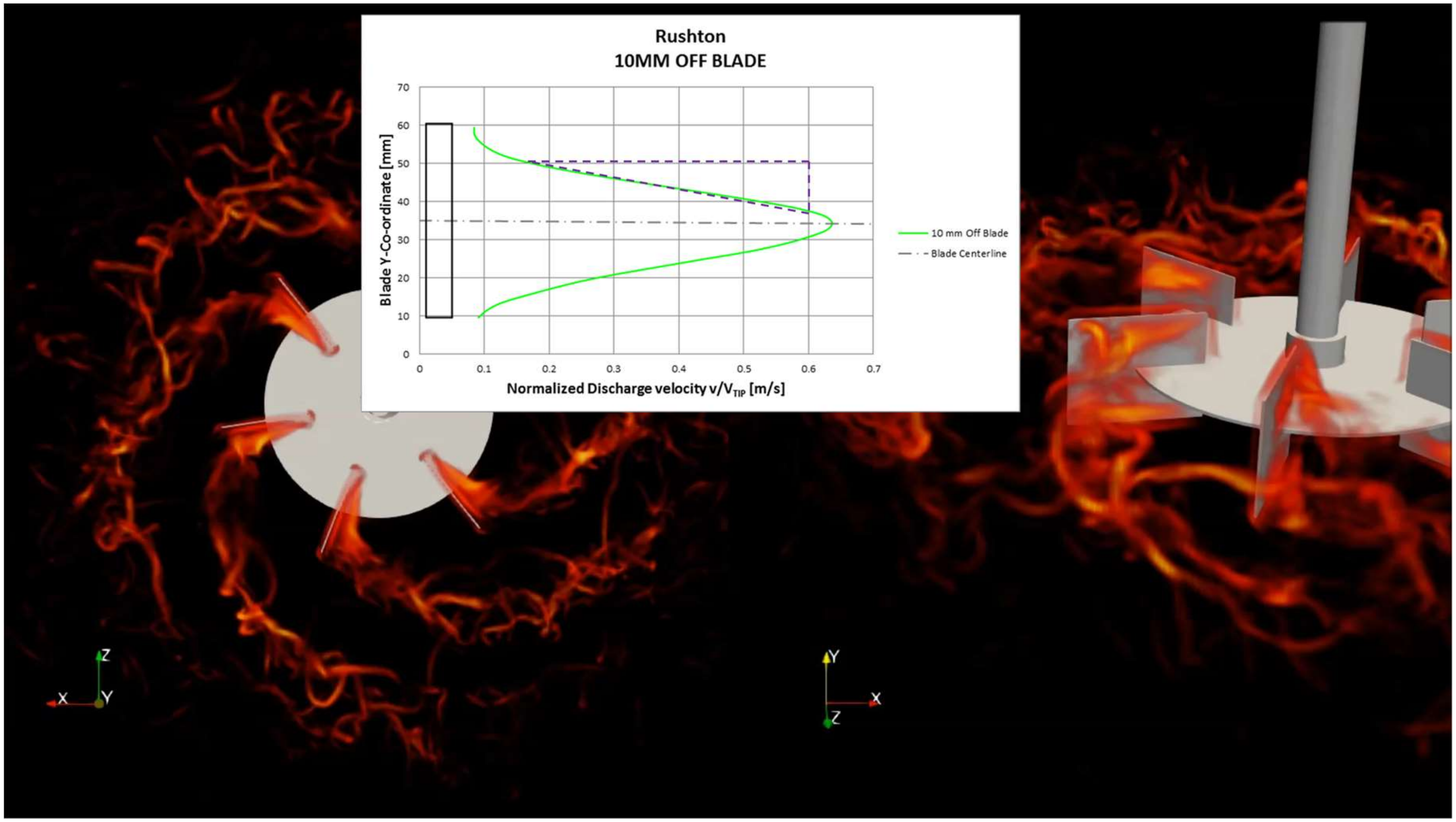
A Constant in Equation (30)
A_{DIS} Discharge area for primary flow from impeller
D Impeller diameter
d_{32} Sauter mean droplet size
Fl Flow or pumping number ($= Q/(ND^3)$)
K Ratio ($= \varepsilon_{MAX}/\bar{\varepsilon}$)
k_{MAX} Maximum kinetic energy in trailing vortex
l_0 Diameter of trailing vortex
N Impeller rotational speed

RUSHTON: PIV → TRAILING VORTEX



PIV by TSI Inc.

RUSHTON: CFD → TRAILING VORTEX



LES CFD using M-Star Simulations LLC DMT

IMPELLER TYPE AND DIAMETER

Easy to estimate mean energy dissipation rate (or power input per unit volume):

$$\bar{\varepsilon} = \frac{P}{M} = \frac{Po}{\pi/4} N^3 D^2 \left(\frac{D}{T}\right)^3$$

B does not experience “mean” conditions

Dissipation is highest in trailing vortex at tip of impeller blades

LOCAL TKEDR AT FEED LOCATION

If dip pipe is used, feeding into impeller suction and vortex behind blade feed will “feel” maximum TKEDR where:

$$\varepsilon_{max} = K\bar{\varepsilon}$$

K has been calculated previously:

$$K = 0.82\frac{x}{Po^{1/4}}\left(\frac{T}{D}\right)^3$$

OPTIMIZING REACTOR OPERATION

Maximize local energy dissipation rate and mean velocity at feed point:

- High power input from motor
- Correct choice of impeller

Use dip pipe to feed into impeller zone

Choose appropriate q_B:

- If necessary, divide feed by using multiple dip pipes

Can reaction rate be slowed?

- Lower temperature? Dilution?

EXAMPLE

Di-Acid + Base $\rightarrow$ Mono-Acidic Product (P) + Water

Mono-Acidic Product + Base $\rightarrow$ Inert By-product (W) + Water

Reaction products are equally soluble:

- Cannot be easily separated

Product sold as solution of P in water.:

- W is inert in product
- Sold on basis of concentration of P

Mixture is diluted to make product:

- Higher P : W ratio → more dilution water added.

LAB STUDIES

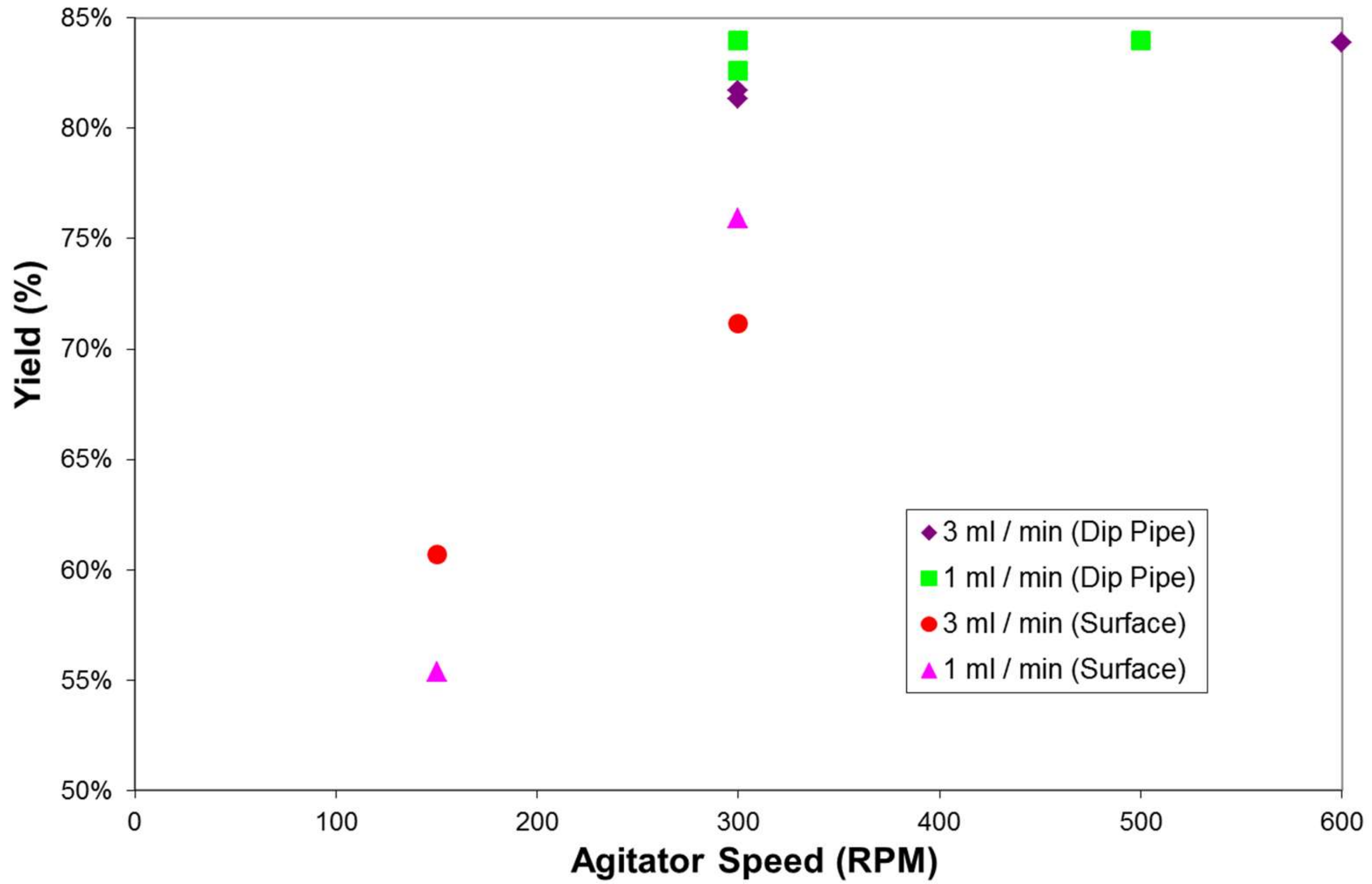
Tests carried out at lab-scale in Hood

If mixing is slow product loses "quality"

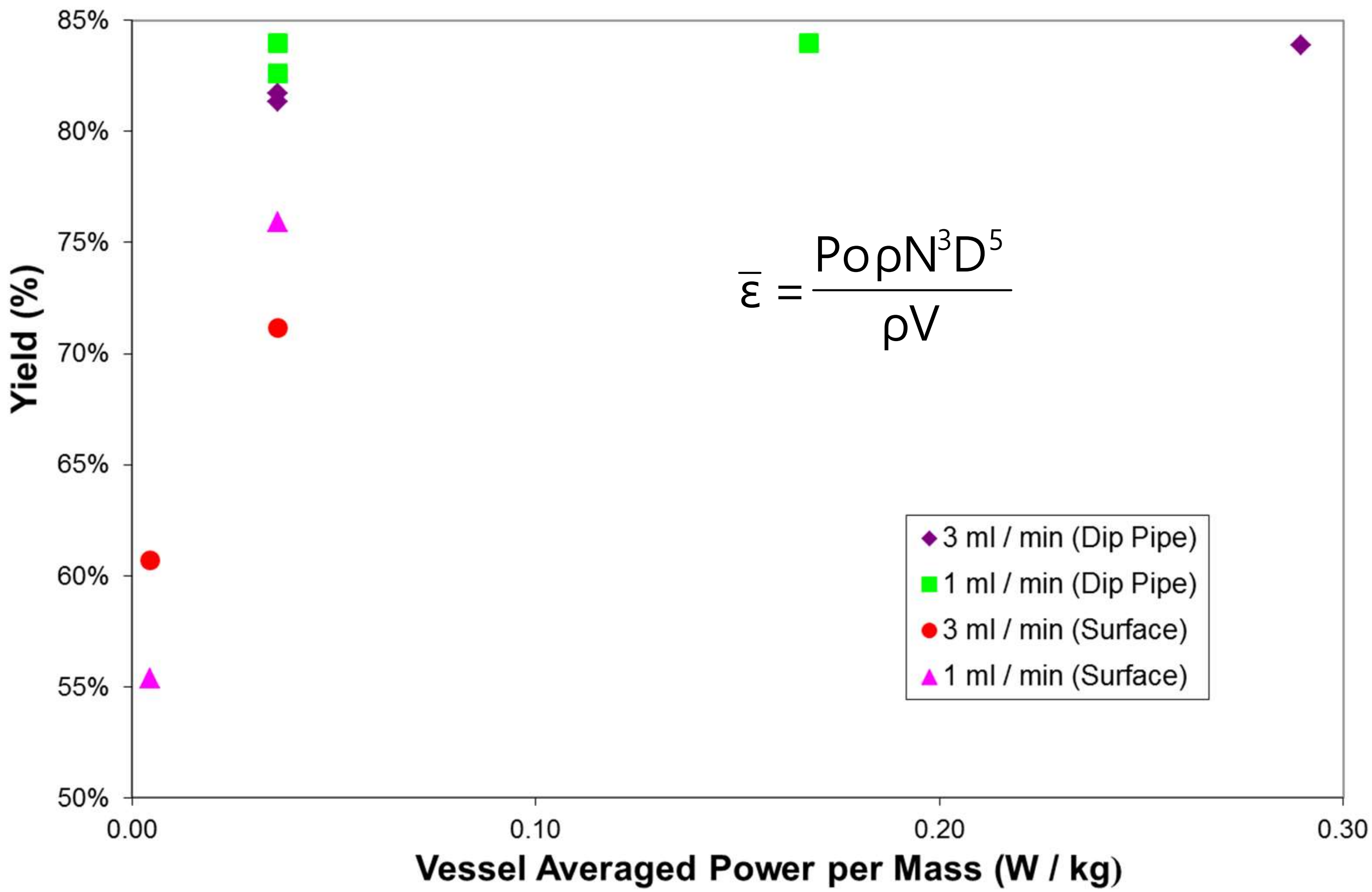
Conditions:

- 1 litre vessel (T = 99 mm) with single Hydrofoil (D = 54 mm)
- Feed rate, q = 1 and 3 ml / min
- Impeller speed = 150 – 600 RPM
- Feed at surface and at impeller tip (through dip pipe)

YIELD vs SPEED

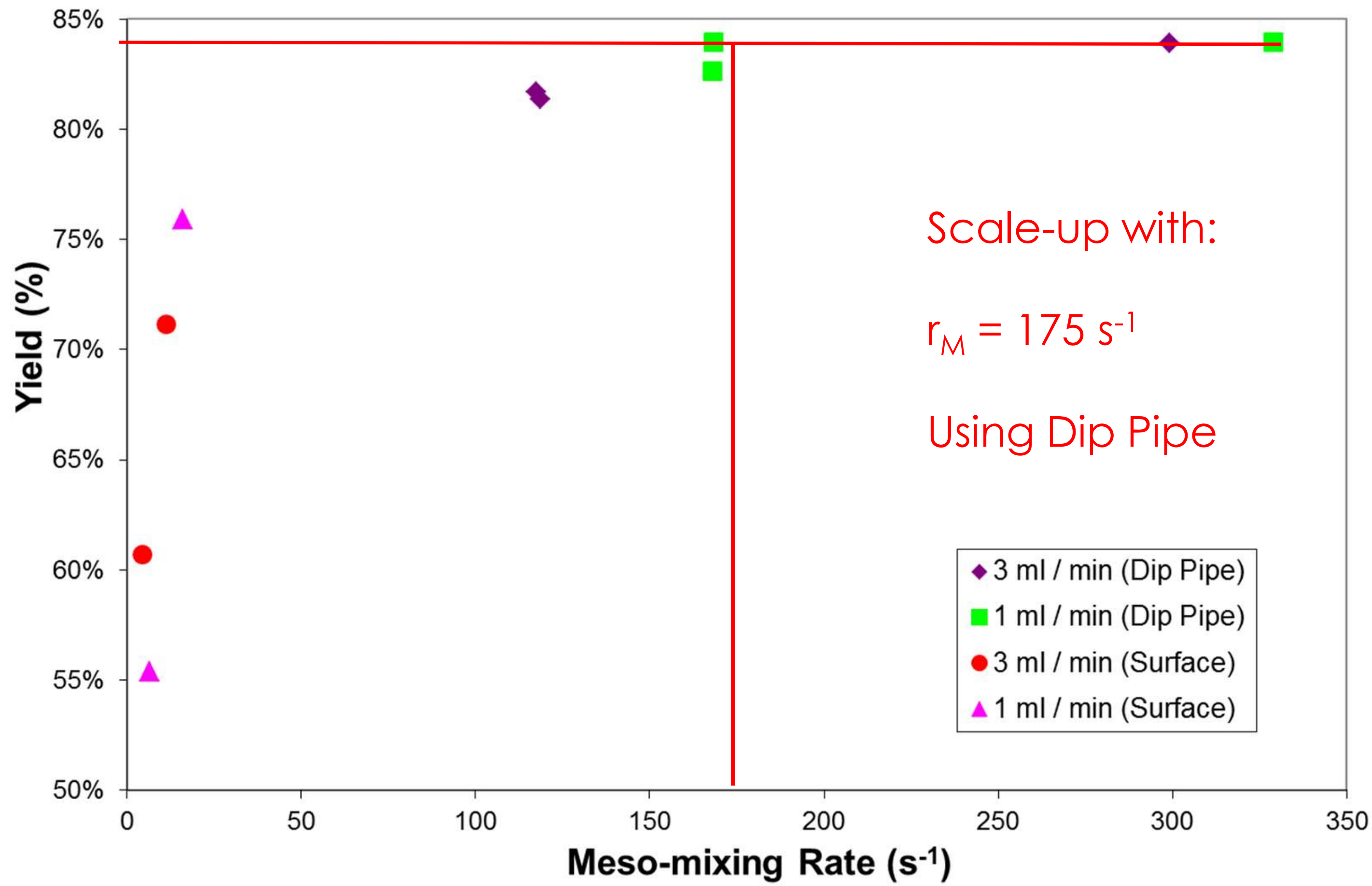


YIELD vs AVG POWER PER MASS

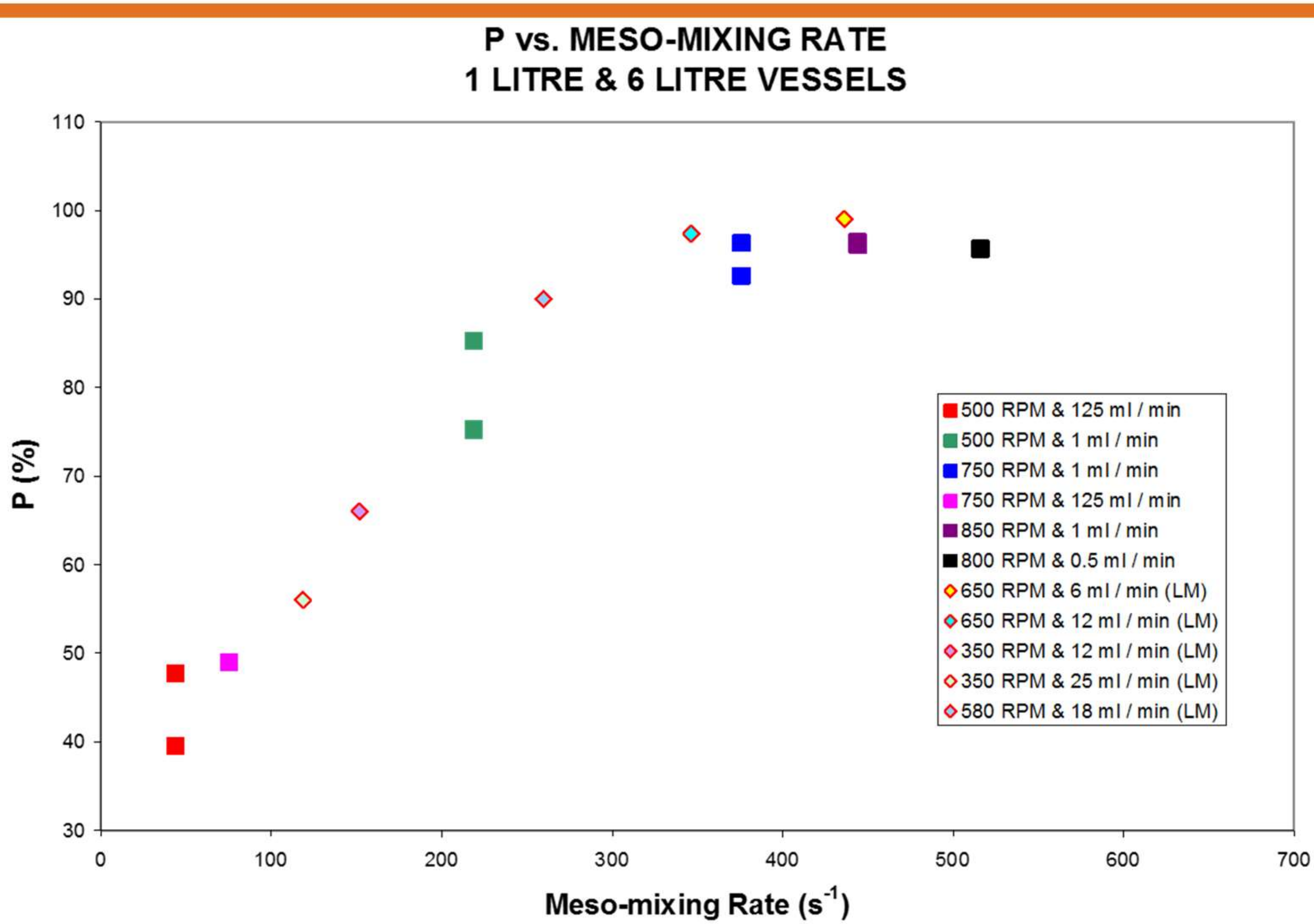


$$\bar{\varepsilon} = \frac{Po\rho N^3 D^5}{\rho V}$$

YIELD vs MESO-MIXING RATE



YIELD vs MESO-MIXING RATE (2)



CONCLUSIONS

Mixing is rarely an issue for:

- Simple reactions
- Slow reactions

Yield of fast, competitive reactions is determined by mixing rate at feed location

In industrial reactors mesomixing timescale controls

Scale-up on constant Damkohler number

Must encourage chemists to run batches that “fail” at lab-scale:

- Find the “knee-of-the-curve”

Alternative chemistry?