Books

1) J.Baldyga & J.R.Bourne "Turbulent Mixing & Chemical Reactions" Wiley (1999)
2) R.O.Fox "Computational Models for Turbulent Reactive Flows" Cambridge U.P. (2003)
3) E.L.Paul, V.A.Atiemo-Obeng & S.M.Kresta "Handbook of Industrial Mixing" Wiley (2004)

CFD Sub-grid Models for Reactive Mixing

Physically based, but not strictly deductive
Reasonable parameter estimates (time constants for mixing at various scales etc.)
Wide range of time- & length-scales (residence/ feed time vs. diffusion time; impeller size vs. λ_B)
Computationally demanding especially SBR when feed volume << volume in vessel

Validation - no adjustable parameters

R.O.Fox - AIChEJ 52(2006)731 : impinging jets
J.Baldyga - Multiple-time-scale model (1989) : compared with expt. for single- & double-feed SBR, CSTR, static mixers & tubular reactors etc.
Ind.Eng.Chem.Res. 44 (2005) 5342
Chem.Eng.Sci. 59 (2004) 1767 etc.

CFD well developed & needs good reaction & precipitation models (reaction scheme etc.) as well as much thermo. & kinetic information.

Competitive / Parallel Reactions

L.Falk et al. Chem.Eng.Sci. 55 (2000) 4233/4245

Solution 1 : KI , KIO_3 , NaOH , H_3BO_3 (o-boric acid), plus alkaline buffer

Solution 2 : H_2SO_4

$$H_2BO_3^- + H^+ \rightleftharpoons H_3BO_3 \quad \text{very fast}$$

$$5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O \quad \text{fast}$$

$$I_2 + I^- \rightleftharpoons I_3^-$$

No segregation — No I_2

Poor mixing — I_2 formed

$$\text{Rate} = k\,[H^+]^2\,[I^-]^2\,[IO_3^-]\,.\,f(\text{ionic strength})$$

Colorimetric analysis for I_3^-

Successive injection of small acid quantities saves time/making-up reagent solutions

Boiling & hot, sparged liquids

John Smith et al. Trans.I.Chem.E.80A (2002) 880

$2OH^- + Cu^{2+} = Cu(OH)_2$ very fast

$OH^- + ester = HO(CH2)_3COO^-$ fast at 100C

{ intramolecular ester = γ-butyrolactone }

Colorimetric analysis of Cu^{2+}

Ungassed,hot sparged & boiling systems studied: stirrer speed, feed position etc.

Pfaudler (retreat-blade) Impeller

Iris Verschuren et al10th European Conf(2000)69

Power & heat transfer well documented

Micromixing studied by neutralization of acid competing with alkaline ester hydrolysis as stirrer speed & feed location varied

Unusual Feed Locations

A.W.Nienow et al. Trans.I.Chem.E.80A (2002)855
LDV,PIV,CFD,Xs all show variation in local eps.
4 feed points & iodine/iodate reactions
Below surface - lowest eps - highest Xs found
Trailing vortex - highest eps - lowest Xs found
(feed pipe fixed very near RT)

Xs segregation index

A.W.Nienow et al. Chem.Eng.Sci.60 (2005) 2333
Feed pipe rotated with RT feeding direct into
trailing vortex - Xs still lower - local eps higher

S.M.Kresta et al.Trans.I.Chem.E. 82A(2004)1153
Surface feed desirable, but eps low/slow mixing
PBTD in usual position, PBTU submerged &
higher on shaft created turbulence near surface
feed-local eps higher/Xs lower than PBTD alone

S.M.Kresta et al. Chem.Eng.Sci. 61 (2006) 3033
High velocity surface jet - local turbulence near
surface & PBTD for general circulation.
Operational difficulties - for example shooting
feed through impeller to tank base where eps
low/Xs high { cf.S.Thoma Diss. ETHZ (1989) }

Scale - up of Static Mixers

R.A.Taylor,W.Roy Penney & Hanh X.Vo

Ind.Eng.Chem.Res. 44 (2005) 6095

12 element Kenics HEM 1/2in,1/4in,1/8in diam.

(1/8in not fully geometrically similar)

Competition for added H^+ between hydrolysis of acetal DMP & neutralization of alkali

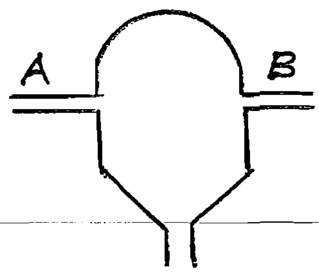
*low flow rate & eps - micromixing - P/V = const.

*high flow rate & eps-mesomixing- res.time=const.

{See also book Worked Ex. 12.1 & 12.4 }

Confined Impinging Jets

B.Johnson& R.Prudhomme AIChEJ 49(2003)2264



A = HCl B = NaOH + DMP

u < 19 m/s μ varied

3 sizes (D) d 0.25,0.5,1.0mm

10 < Rej <3500

DMP (5-320ms) & Ester (350ms)

hydrolyses vs. neutralization

{CFD - Y.Liu & R.Fox AIChEJ 52 (2006) 731 & D.L.Marchiaso et al. Chem.Eng.Sci. 62 (2007) 2228 }

Reactive mixing principles — experimental plan & general scaling correlation — validated scale-up

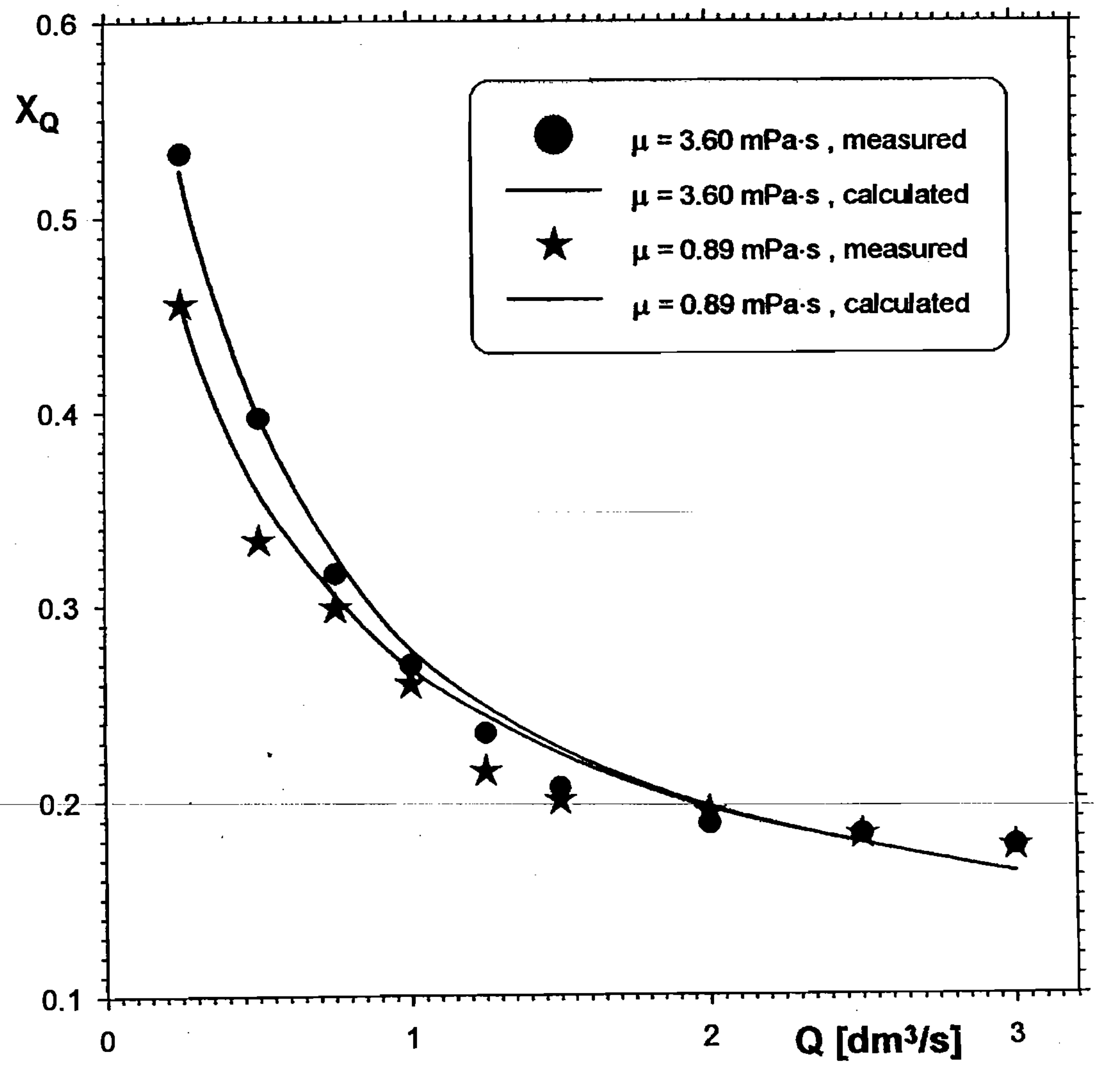
Fast (few ms) for nanoparticles & mixing-free rxns.

$$\tau_{mix} \sim \frac{\nu^{1/2}}{\epsilon^{1/2}} \sim \frac{\nu^{1/2}\, d^{1/2}\, D^{3/2}}{u^{3/2}\, d^{3/2}}$$

$$\tau_{mix} \not\propto u^{-1} \qquad \tau_{mix} \not\propto \nu^{3/2}$$

3.18 Predicted and measured yields (X_Q) at two viscosities and various flow rates: identification of micro- and meso-mixing regimes

Fig 14



$$\epsilon \sim Q^3 \qquad L_c \neq f(Q)$$

$$\tau_E \sim \sqrt{\frac{\nu}{\epsilon}} \sim Q^{-1.5} \qquad \tau_S \sim \left(\frac{L_c^2}{\epsilon}\right)^{1/3} \sim Q^{-1}$$

Microchannel mixers / Microreactors

Laminar flow↔laminated structure (μm-scale)

t (99% complete)≈ L^2 / D {L=10μm ,t=100ms}
Generally t≈10ms - 1 s
V.Hessel et al AIChEJ 49 (2003) 566 {10ms}
V.Hessel et al Org.Proc.R&D 8(2004)511 {100ms}
K.F.Jensen et al Ind.Eng.Chem.Res.44(2005) 2351 {25ms}
H.Löwe et al Org.Proc.R&D 10(2006)1144 {5ms}

Multiple reactions (Xs,I_2) used ONLY to rank different mixer designs
V.Hessel et al Ind.Eng.Chem.Res.38(1999)1075
J.Yoshida et al Chem.Comm. (2003) 354
M.A.Schneider et al Chem.Eng.J.101(2004)241
B.Werner et al Chem.Eng.Technol.28(2005)401

Examples of designs for faster micromixing

1)V-micro-jetmixer - patented by Bayer(St.Ehlers et al Chem.Eng.& Proc.39(2000)291)
2)Microsegment collision (K.Mae et al Chem.Eng. Technol.28(2005)324)

Need for detailed application of test reactions to assess micromixing quantitatively & determine time constant(s).

Comparisons between microreactors & conventional equipment have sometimes been biased ! (lab.vessel with mag.stirrer & no baffles)

Micromixing in two - phase system
D.Brilman et al. Chem.Eng.Sci. 54 (1999) 2325
Is micromixing in continuous phase influenced by dispersed phase ?
Diazo coupling of 1- & sometimes 2-Naphthol with diazotized sulfanilic acid (25 C & pH = 9.9)
G/L 7% hold-up: increase in eps near surface & decrease near RT- small effects.{Fort;book p.692}
S/L glass beads - few% no effect BUT 40wt% damped turbulence slightly.{C.Bennington - abs/ adsorption on fibers - difficult experiments}
L/L 40vol% Heptane : damping just like solids.
Octanol extracted 1-N,then returned it to aq. phase.Reactions spread to bulk - lower eps & higher Xs than at feed point.
E-Model good when density & viscosity corrected for dispersed phase.
Study fast reactions & extraction further.

PTC
G.D.Yadav et al.Ind.Eng.Chem.Res.44(2005)1273
L/L PTC alkylation : competitive/consecutive rxns with primary product required.
Large field for further study (L/L, S/L/L etc)

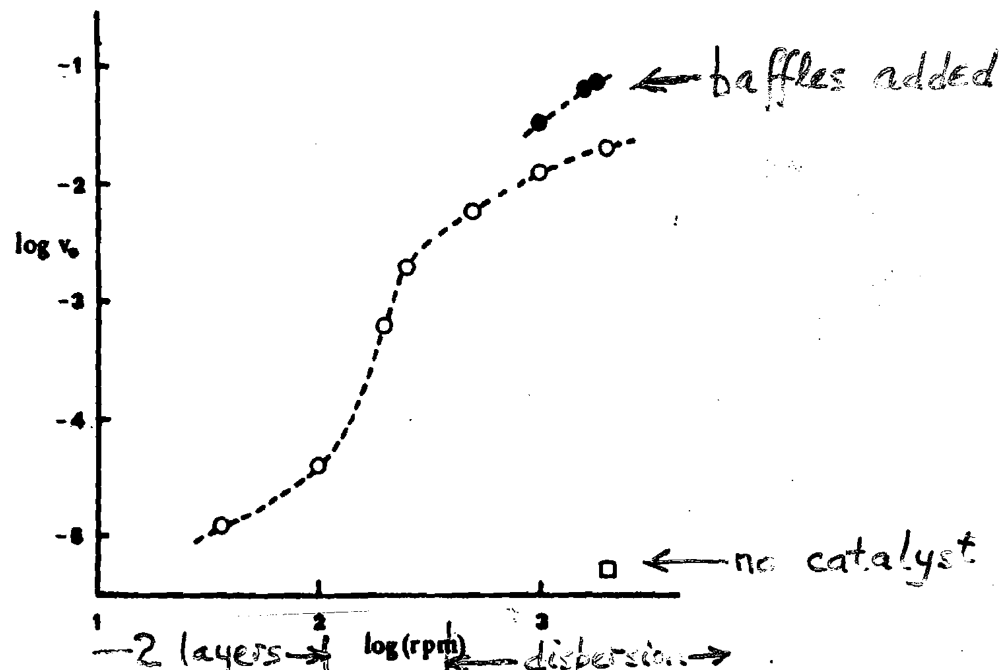
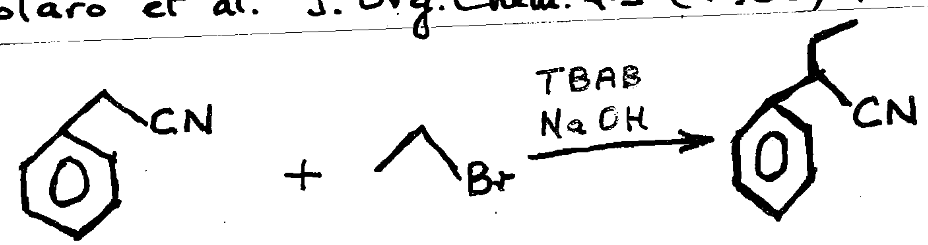


Figure 1. Dependence of the initial rate of disappearance of PAN (v_0) on the stirring rate (revolutions per minute): ○, runs P1–P7 carried out in a round-bottom flask; □, run P8 carried out in the absence of TBAB; ●, runs R1–R3 carried out in a high-mixing-efficiency reactor.

{R. Solaro et al. J. Org. Chem. 45 (1980) 4179}



cf. same PTC alkylation in supercritical C_2H_6

{C. Wheeler et al. Ind. Eng. Chem. Res. 41 (2002) 1763}

L/L Reactions & Selectivity

J.F.King et al. JACS 114 (1992) 3028

Acylation of Benzylamine (PhCH2NH2) with Benzoyl Chloride (PhCOCl) : kinetics available.

Amine (pK=9.3) reactive when pH > pK

Aryl Chloride hydrolyzed by Water (t1/2 = 380ms) & by OH^- - requires low pH.

Optimized pH = 10.4 (buffered)

Principal rxn "fast" (mainly in aq.diffusion film)

Wasteful hydrolysis also in film with weak agitation,BUT "slow" in bulk with strong stirring to secure high selectivity.

Scope for further study !

Stabilization of MMA polymerization in scCO2

M.Morbidelli et al. Macromol.37 (2004) 2996

Surfactant/dispersant reversibly attached to precipitating polymer (weak H-bonds etc.)

N < 25rpm d~2µm fluffy powder Mw~450000

N > 45rpm tacky coagulate low Mw & yield

Data on conversion, MWD, polymer form/SEM

Rxn occurs in both phases

Stabilizer shear-sensitive - change it or mixer ?

Screening Experiments in Chemical Development

J.R.Bourne Org.Proc.R & D 7 (2003) 471

Glass vessel : ~1litre, baffles, standard impeller

Vary N 100 - 1000rpm — **No** — **Mixing not critical**

Effect on products

Vary feed rate / time — **No** — **Micromixing**

Effect

Vary feed position — **No** — **Macromixing**

Effect

Mesomixing

{ **Vary number of feed points** — **No** — **Micromixing**

Meso- / Macromixing }

[**Vary viscosity** — **No** — **Meso- / Macro-mixing**

Micromixing]