中国科学院过程工程研究所
Institute of Process Engineering, Chinese Academy Of Sciences

China-USA: Towards Competitive Sustainable Manufacturing through Collaboration, 2014

Numerical Simulation of Multiphase Reactors/Crystallizers and Application for Green Processes and Sustainable Development

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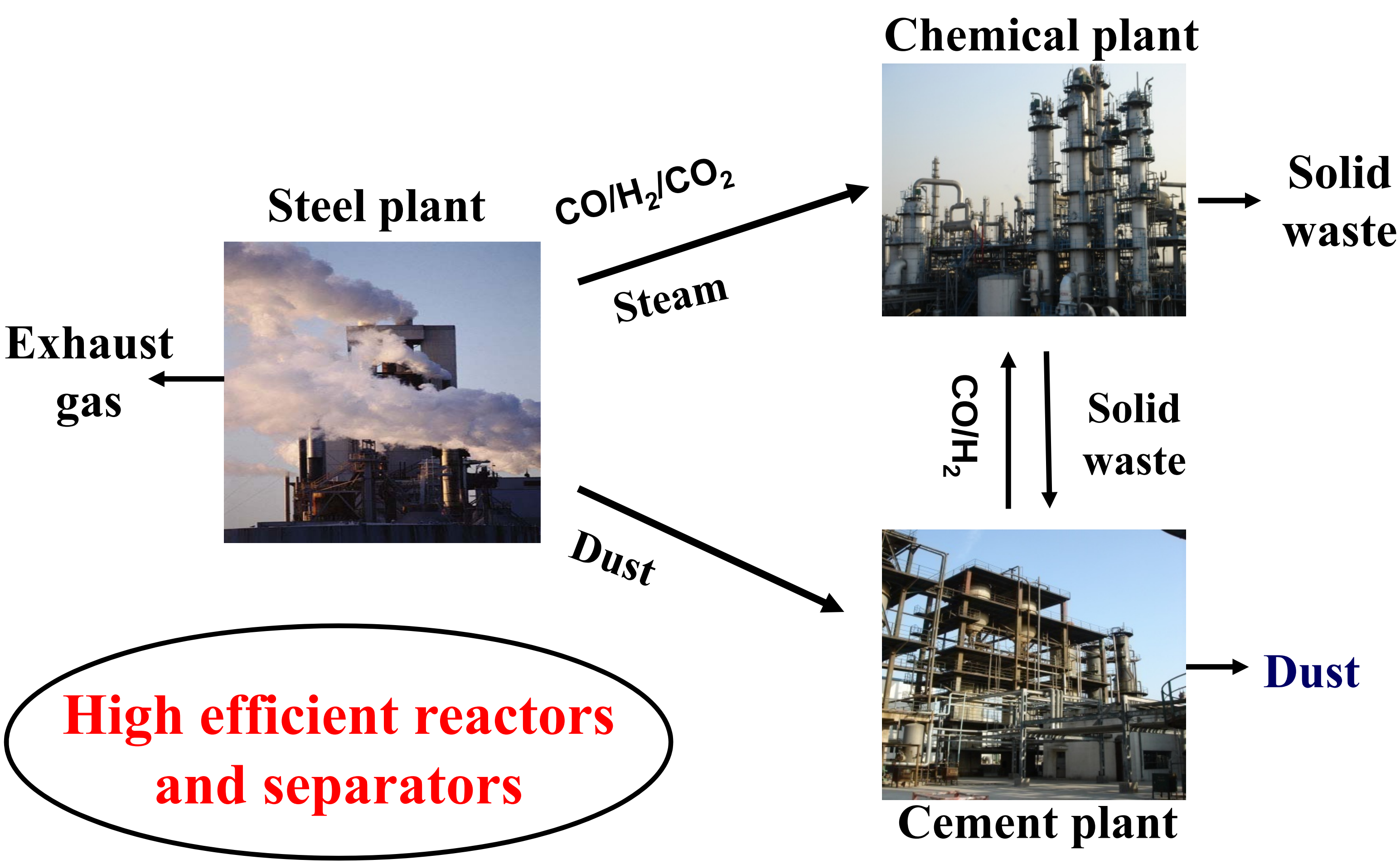
Outline

- Introduction
- Models and numerical methods
- Simulated results
- Industrial applications
- Perspective
- Acknowledgements

Background

Industrial high energy and material consumption and heavy pollution

Example: develop a sustainable and ecological industrial chain



Related with the national sustainable and ecological development

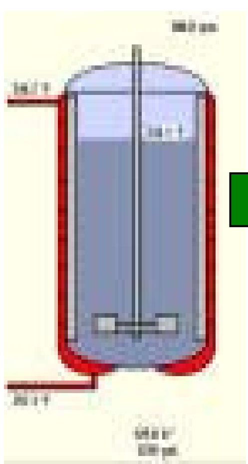
Process Industry: reactors (CFD)

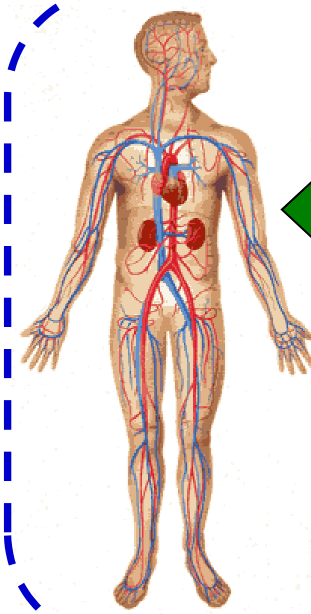
A multiphase reactor is to a process plant
what heart / liver are to human body

It is important to know what is going on inside

- **Multiphase flow**
- **Heat and mass transfer**
- **Chemical reaction**

Black box
Vs.
CFD



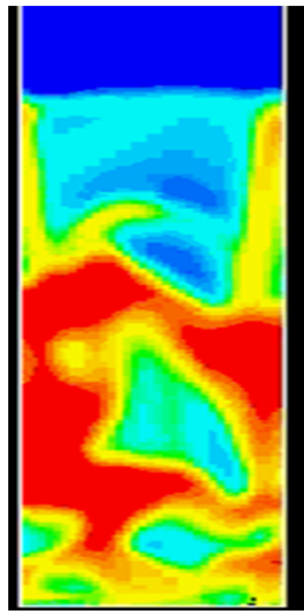


Design, scale-up, diagnosis, optimization and manipulation of multiphase reactors

High material and energy consumption and pollution emission

Low transport efficiency and reaction yield in industrial reactors: react before sufficiently mixed

Scale-up effects of reactors, separators and processes



many inefficient reactors in China plants

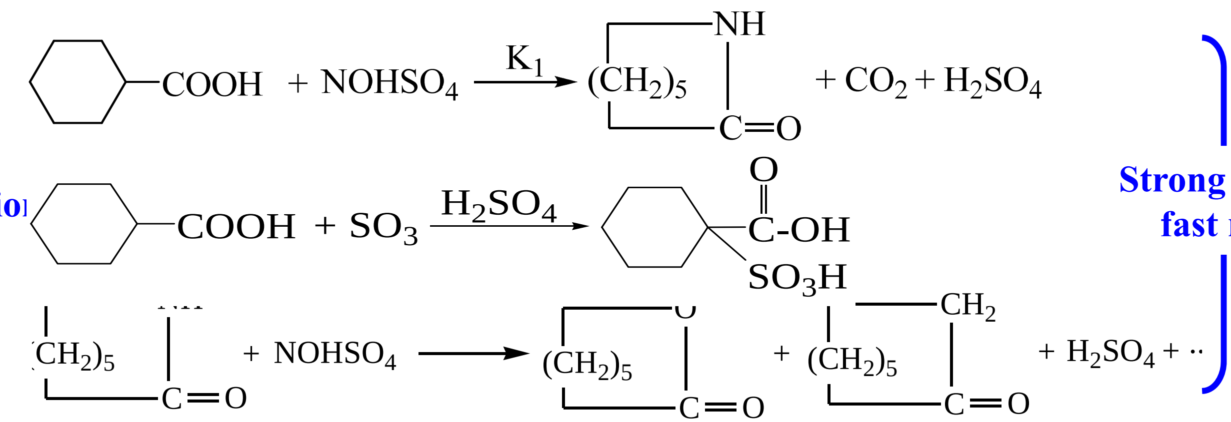
Industrial example

Amidation: gas-liquid-liquid stirred reactor

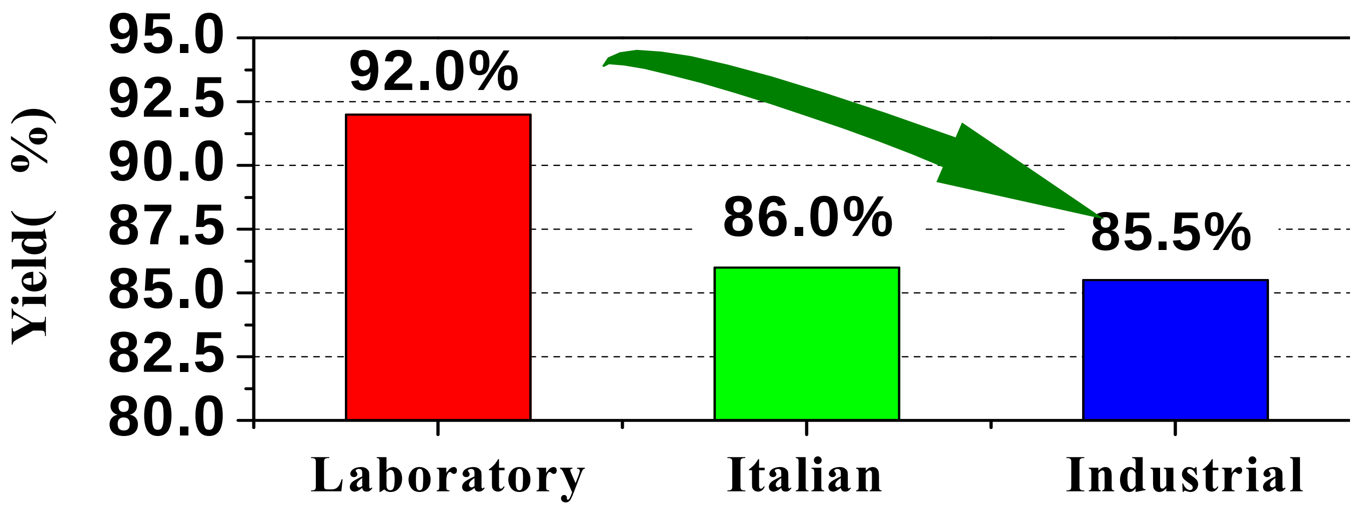
Main reaction

Parallel side reaction

Consecutive side reaction



Strong exothermic fast reactions



(SINOPEC)

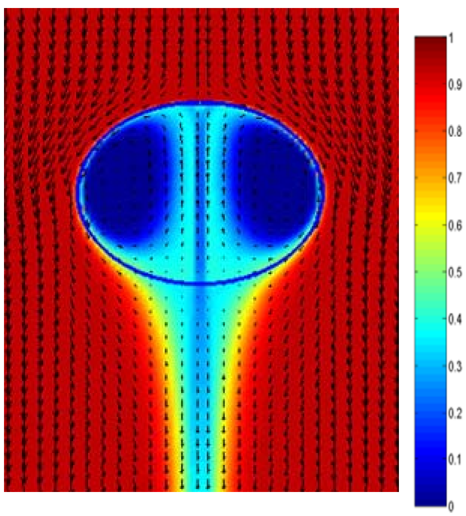
- Inhomogeneity at small scales
- Transport intensification

Industrial reactor 27,000 L, 100,000 times of laboratory scale

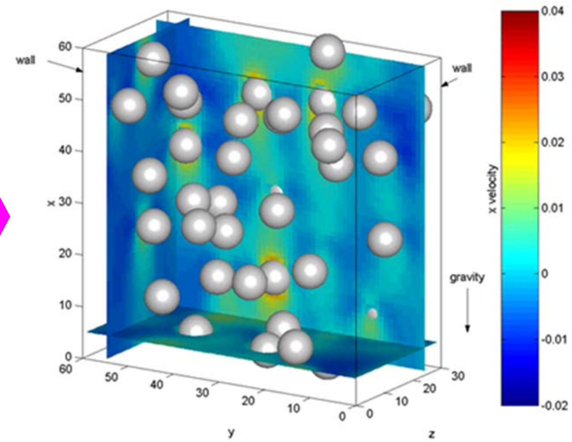
Fast reactions, rapid molecular mixing, restricted by multiphase transport

Mathematical model and numerical simulation

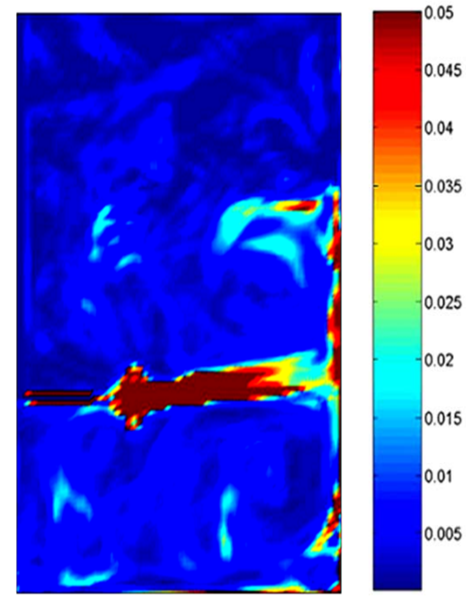
Understand the nature of flow, mixing and heat/mass transfer at different scales



Particle (drop, bubble) scale



Particle assemblage (drop swarms) scale



Reactor scale

Particle-fluid and particle-particle ⟺ Closed model (sub-model, small scale model)

Molecule ⟺ Sub-particle ⟺ Single particle ⟺ Particle assemblage ⟺ Reactor ⟺ Process

Multiple-scale method and coupled algorithm

Green Process and Engineering: High efficient reactors

- reduce the number and size of equipments
- intensify mass and heat transfer
- reduce by-products

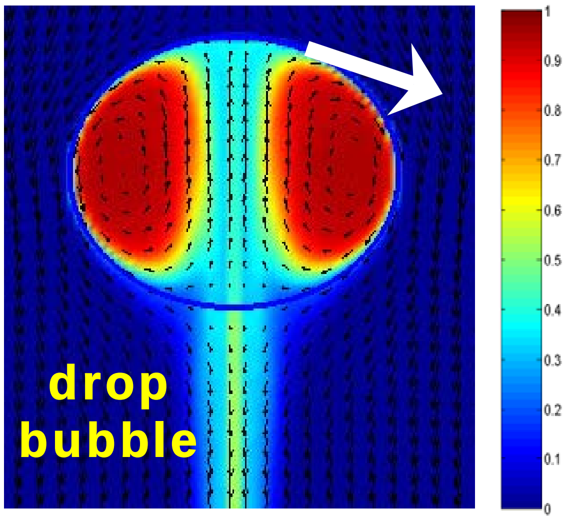
Purpose

- Develop multi-scale reactor model and high efficiently numerical method
- Understand the mechanism of multiphase flow, mixing and transport
- Develop high efficient reactors to save energy/materials and reduce emission
- Aim at a green process and engineering and sustainable industries

Particle scale

Particle (drop, bubble) model and transport intensification

Concentration transformation method – overcome calculation difficulty in discontinuous interface concentration for level set approach



$$N_A = k\,a\,(C_2 - C_1)$$

Interface condition

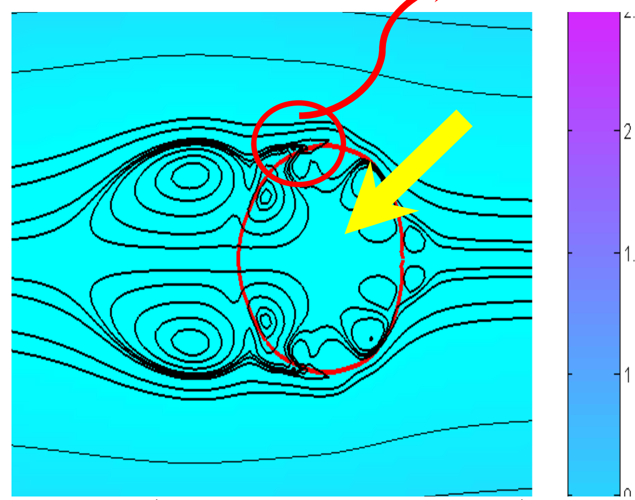
$$C_2 = mC_1$$

$$(m \neq 1,\ C_2 \neq C_1)$$

$$D_1 \frac{\partial C_1}{\partial n_1} = D_2 \frac{\partial C_2}{\partial n_2}$$

increase mass transfer coefficient

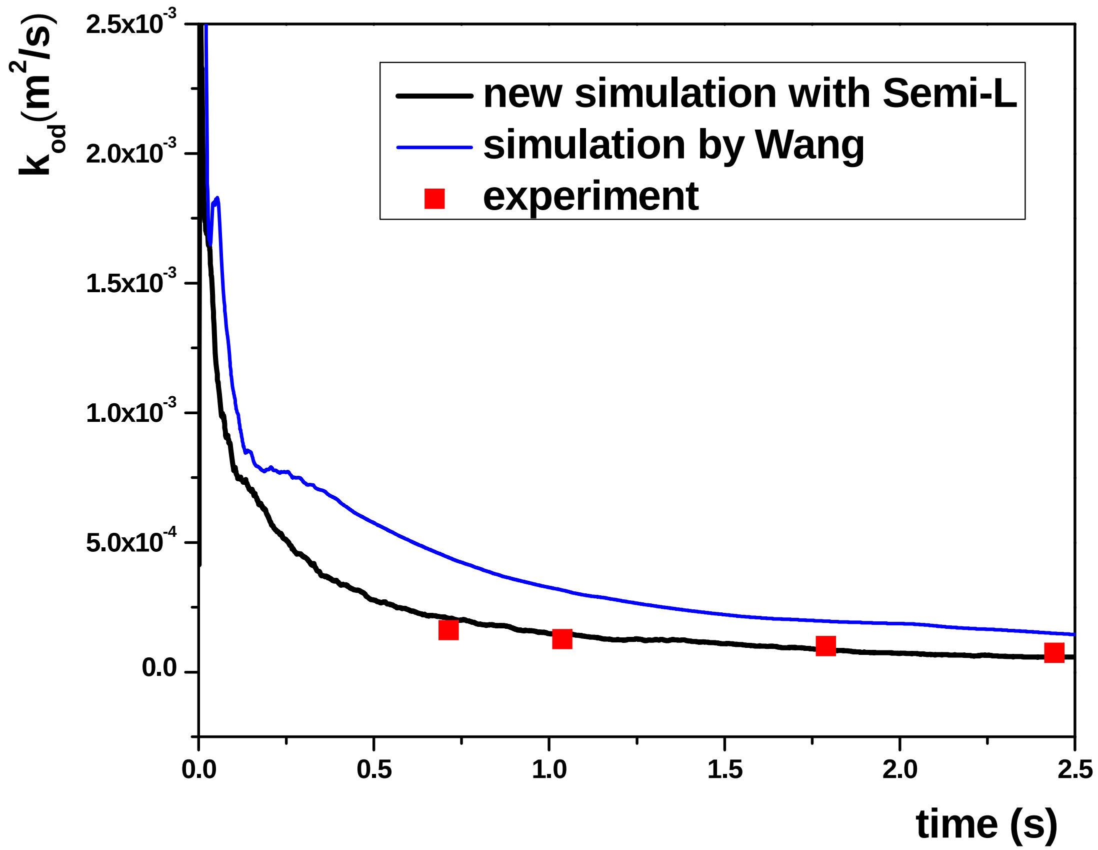
surfactant



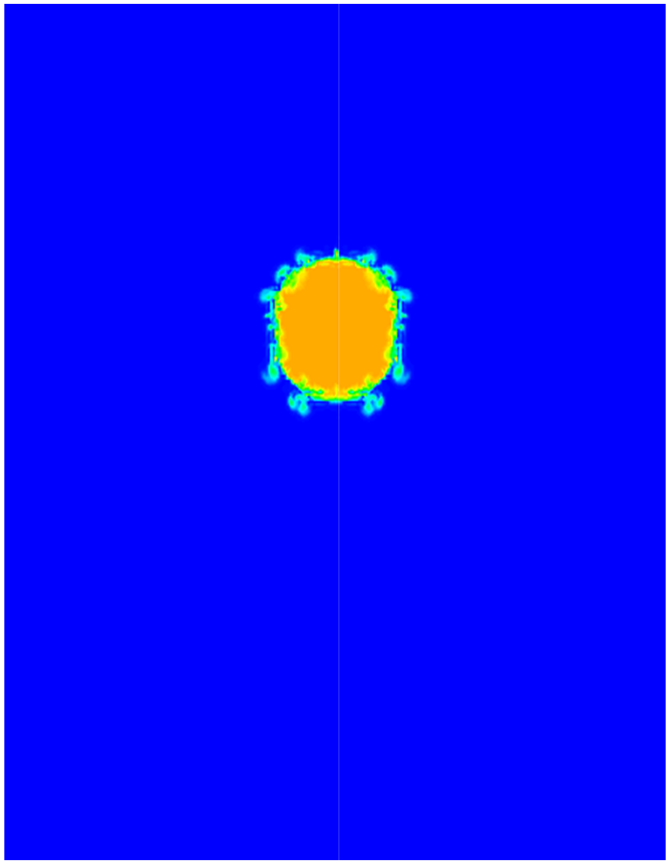
$$\mathbf{F}_{\mathrm{Ma}} = \left(\sigma\kappa\mathbf{n} - \frac{\partial \sigma}{\partial c}(\mathbf{I} - \mathbf{nn}) \cdot \nabla c \right) \delta(\phi)$$

Wang et al., *AIChE Journal*, 2013, 59(11), 4424-4439
Wang et al., *AIChE Journal*, 2011, 57(10), 2670-2683
Wang et al., *Chem. Eng. Sci.*, 2011, 66: 2883-2887
Lu et al., *Chem. Eng. Sci.*, 2010, 65(20): 5517-5526
Wang et al., *Chem. Eng. Sci.*, 2008, 63(12), 3141-3151
Yang & Mao, *Chem. Eng. Sci.*, 2005, 60, 2643-2660

Marangoni effect on a moving deformable drop



Predicted overall mass transfer coefficients versus experimental ones （$c_{d,0}$=7.75wt%）

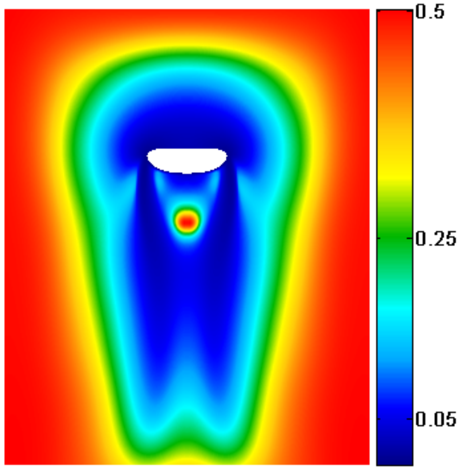


Contour distribution of concentration field

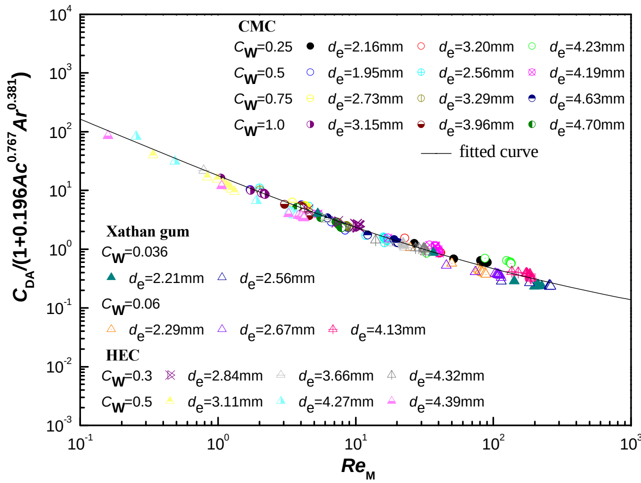
Wang et al., *AIChE Journal,* 2011, 57(10), 2670-2683

Numerical simulation of unsteady motion and dissolution of bubble

in Newtonian and non-Newtonian fluids

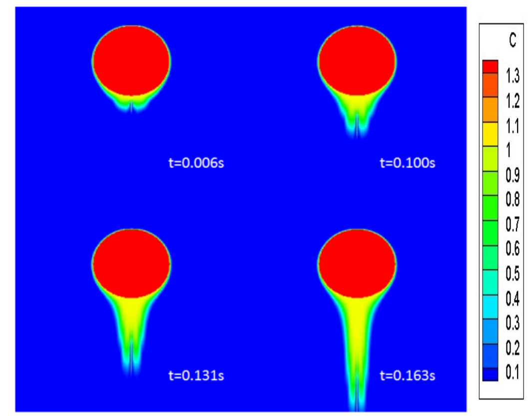


Distribution of viscosity around a bubble in non-Newtonian fluid (Re_M=80.9)



Drag coefficient for unsteady motion

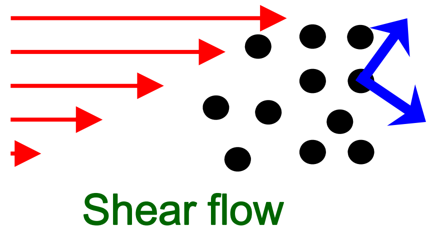
$$C_{DA} = \frac{16}{Re_M}\left(1+0.12Re_M^{0.6}\right)\left(1+0.196Ac^{0.767}Ar^{0.381}\right)$$

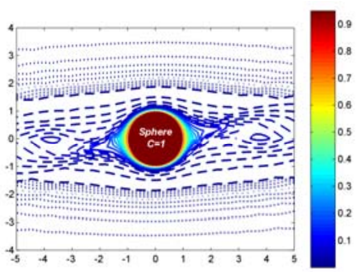


Concentration evolution of CO_2 bubble dissolving in 1% CMC aqueous solution (shear-thinning)

Chen et al., submitted to *Chem. Eng. Sci.*, 2013;
Zhang et al., *J. Non-Newtonian Fluid Mech.*, 2010, 165: 555-567;
Zhang et al., *Chem. Eng. Sci.*, 2008, 63: 2099-2106;
Zhang et al., *Ind. Eng. Chem. Res.*, 2008, 47: 9767–9772

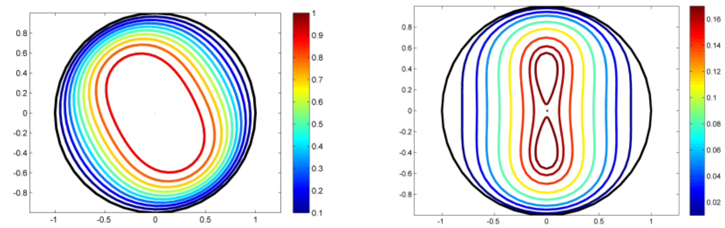
Mass/heat transfer of suspended particles in shear/extensional flows





Sc=10000,
Re=1,
Pe=10000
concentration
contours

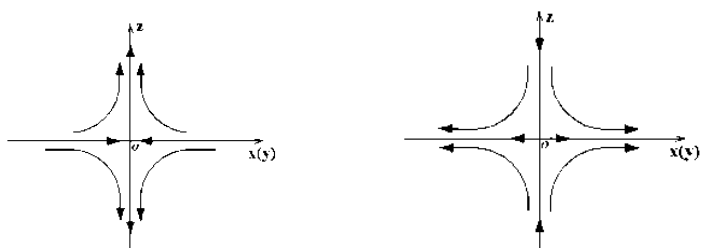
$$Nu = \frac{1}{\lambda+1}\left(0.2066Pe_1^{1/2} - 0.2007\right) + 0.4670Pe_1^{1/2} + 1.0533$$



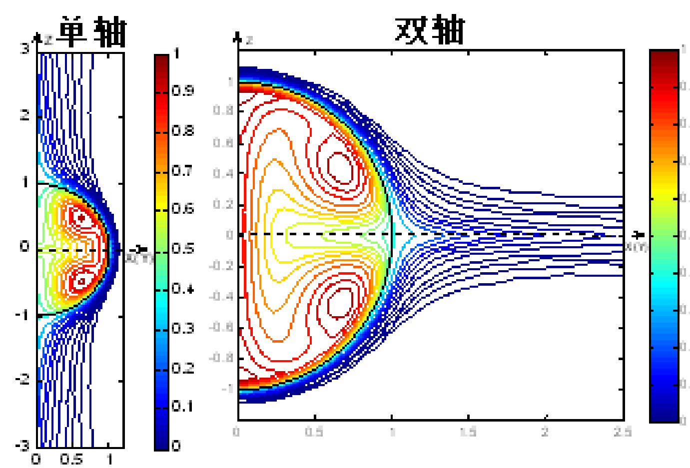
Contours of solute concentration inside a drop

Pe_2 =50, Fo=0.03 Pe_2 =50000, Fo=0.17

Yang et al., *AIChE Journal*, 2011, 57(6), 1419-1433
Subramanian et al., *J. Fluid Mech.*, 2011, 674, 307-358
Li et al., *AIChE Journal*, 2014, 60(1), 343-352



concentration contours for conjugate mass transfer from a drop immersed in uniaxial and biaxial extensional flows (Pe_1=1000, K=1, m=1, λ=1, Fo=0.01)



Zhang et al., *AIChE Journal*, 2012, 58, 3214-3223
Zhang et al., *Chem. Eng. Sci.*, 2012, 79, 29-40

Transport intensification at small scales

Reactor scale

Models and coupled modeling methods for multiphase reactors

Governing equations

- **based on phase interaction, mixing and transport mechanism (small scales)**
- **coupled modeling of multiphase flow, transport and reaction: high-order scheme and coupled algorithm (reactor scale)**

Multiphase flow

$$\frac{\partial}{\partial t}\left(\rho_m \bar{\alpha}_m \bar{u}_{mi}\right)+\frac{\partial}{\partial x_j}\left(\rho_m \bar{\alpha}_m \bar{u}_{mi} \bar{u}_{mj}\right)=$$

$$-\frac{\partial\left(\bar{p}_m\right)}{\partial x_i}+\rho_m \bar{\alpha}_m g_i+\bar{F}_{mi}+\mu_m \frac{\partial}{\partial x_j}\left(\frac{\partial\left(\bar{\alpha}_m \bar{u}_{mj}\right)}{\partial x_i}+\frac{\partial\left(\bar{\alpha}_m \bar{u}_{mi}\right)}{\partial x_j}\right)-\frac{\partial\left(\rho_m \bar{\alpha}_m \tau_{mij}\right)}{\partial x_j}$$

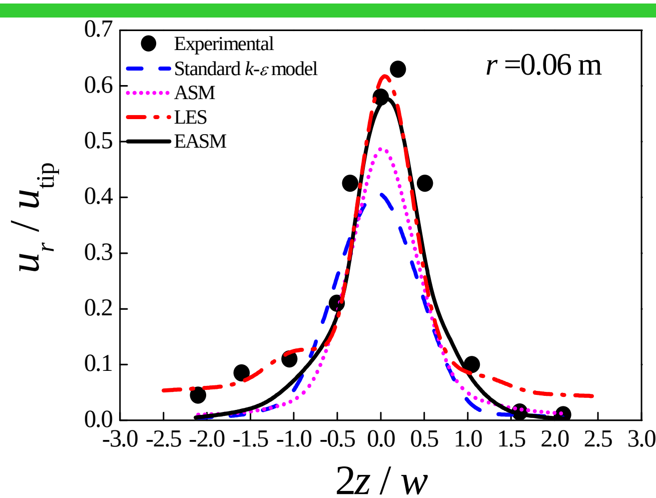
$$F_{\mathrm{m}i}=\frac{3 \alpha_{\mathrm{c}} \alpha_{\mathrm{m}} C_{\mathrm{D}}\left|\mathbf{u}_{\mathrm{m}}-\mathbf{u}_{\mathrm{c}}\right|\left(u_{\mathrm{c}i}-u_{\mathrm{m}i}\right)}{4 d_{\mathrm{m}}}+C_{\mathrm{vm}} \alpha_{\mathrm{m}} \rho_{\mathrm{c}}\left(u_{\mathrm{c}j} \frac{\partial u_{\mathrm{c}i}}{\partial x_j}-u_{\mathrm{m}j} \frac{\partial u_{\mathrm{m}i}}{\partial x_j}\right)+C_{\mathrm{lift}} \alpha_{\mathrm{m}} \rho_{\mathrm{c}}\left(\varepsilon_{ijk} \varepsilon_{kl\mathrm{n}} u_{\mathrm{m}j} \frac{\partial u_{\mathrm{c}n}}{\partial x_l}-\varepsilon_{ijk} \varepsilon_{kl\mathrm{n}} u_{\mathrm{c}j} \frac{\partial u_{\mathrm{c}n}}{\partial x_l}\right)$$

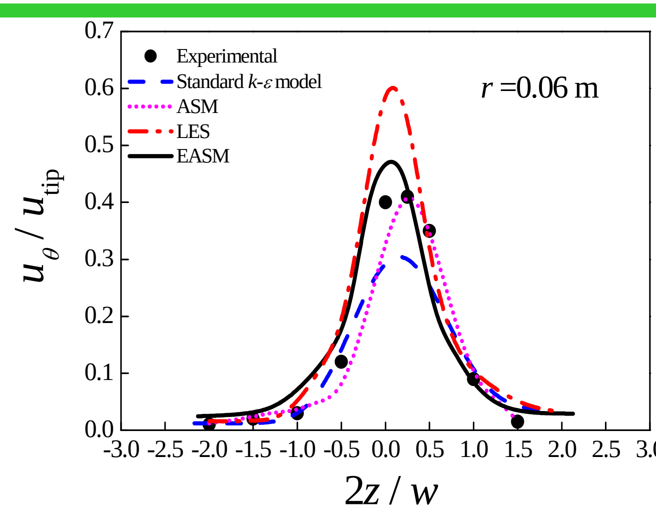
$$\tau_{\mathrm{m}ij}=-\frac{2}{3} \delta_{ij} \mu_{\mathrm{m}} \frac{\partial u_{\mathrm{m}j}}{\partial x_j}+\mu_{\mathrm{m}}\left(\frac{\partial u_{\mathrm{m}j}}{\partial x_i}+\frac{\partial u_{\mathrm{m}i}}{\partial x_j}\right)$$

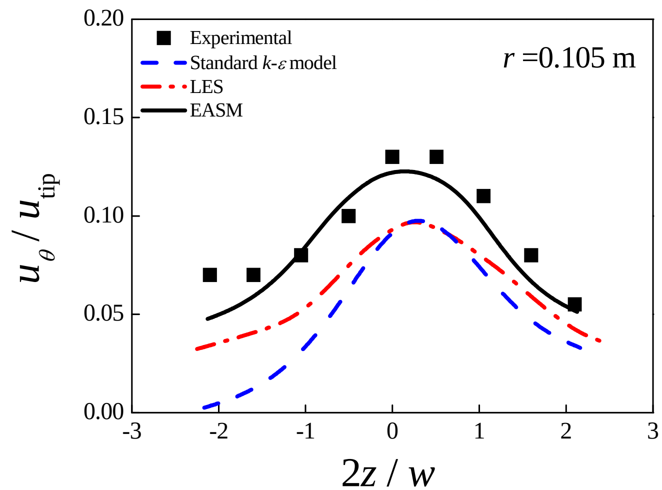
Convection-diffusion mass/heat transfer

$$\frac{\partial(\alpha_k \rho_k C_k)}{\partial t}+\underline{\nabla \cdot \alpha_k \rho_k C_k U_k}=\underline{\alpha_k \rho_k S_k}+\underline{\nabla \cdot \alpha_k \rho_k\left(J_k+c_k^{\prime} u_k^{\prime}\right)}+\rho_k C_k m_k+\rho_k L_k$$

Explicit algebraic stress model for stirred tanks







Model	Turbulent flow	CPU time
Standard *k-ε* model	Isotropy	10 hours
EASM	Anisotropy	16~18 hours
LES	Anisotropy	30 days

(a case with 800,000 control volumes)

Profiles of velocities at different radial positions (*T*=0.27 m, *H*=*T*, *D*=0.093 m, *C*=*T*/3, *N*=200 rpm)

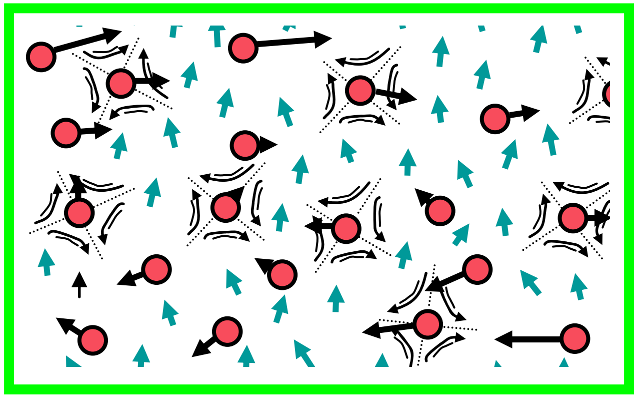
Feng et al., *Chem. Eng. Sci.*, 2012, 69, 30-44

Feng et al., *Chem. Eng. Sci.*, 2012, 82, 272-284

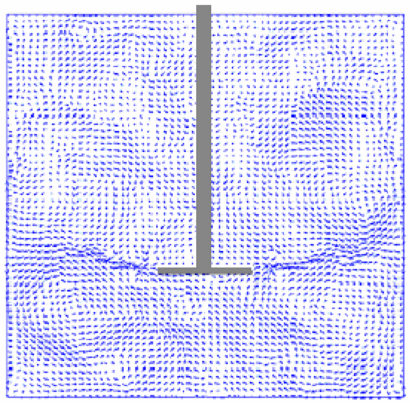
Feng et al., *Chem. Eng. Res. Des.*, 2013, 91(11), 2114-2121

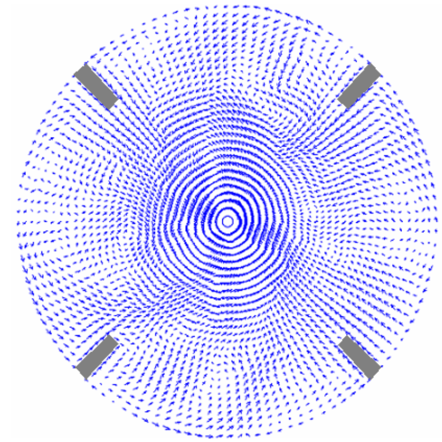
Euler-Euler large eddy simulation of turbulent flow

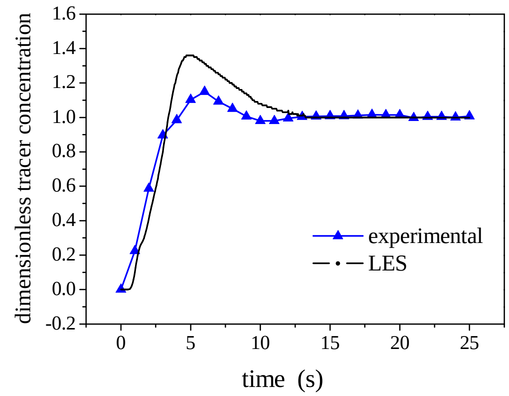
Euler-Lagrange model



	Holdup	Computing speed
Euler-Lagrange	<1%	slow × high holdup
Euler-Euler	>10%	several times faster
Industrial system	10~50%	







Concentration distributions of tracers at different time by LES at N=6.67 s^{-1} (C=T/3, Q_G=1.67×10^{-4} $m^3 \cdot s^{-1}$)

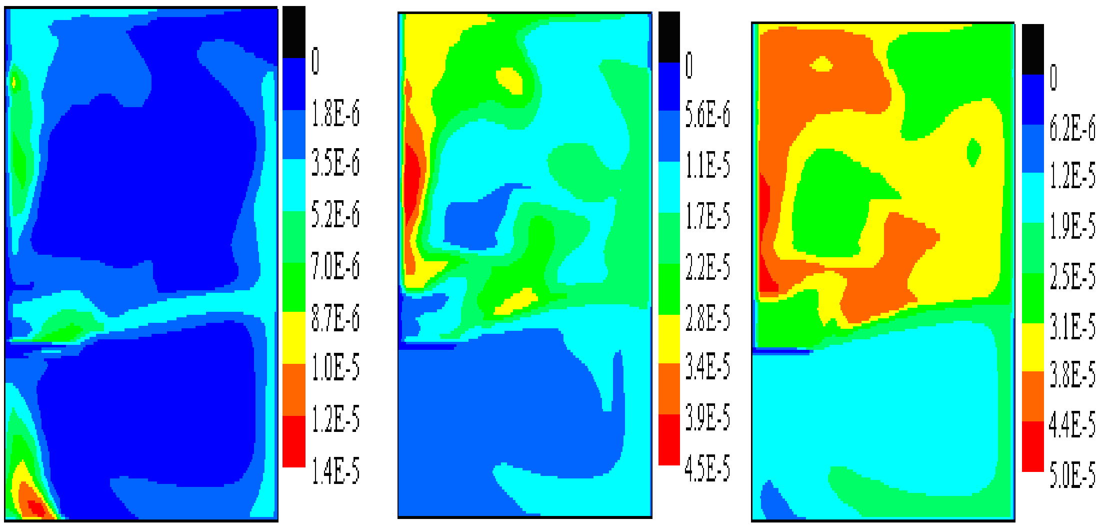
Zhang et al., *AIChE Journal*, 2008, 54: 1963-1974

P. Schwarz at CSIRO [*J. Comput. Multiphase Flows*, 2010, 2: 165]: "first attempt", "good idea"; [*Chem. Eng. Sci.*, 2011, 66: 3071]: " significant promise"

Zhang et al., *Industrial & Engineering Chemistry Research*, 2012, 51, 10124-10131

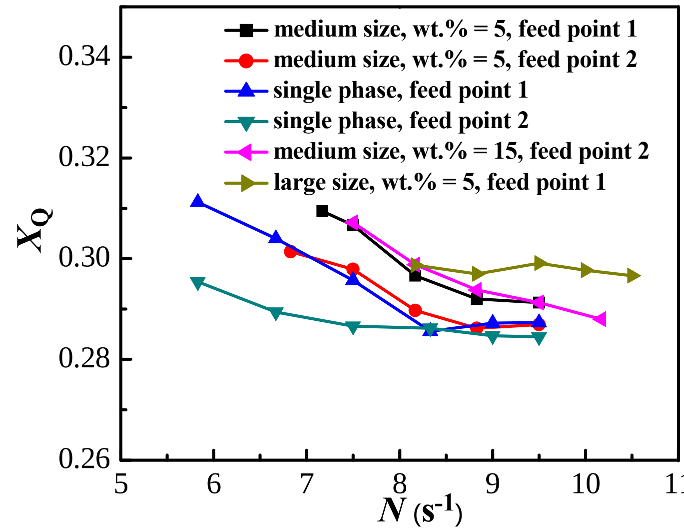
Macro-and micro-mixing in multiphase reactors

Fast reactions (transport controlled)



t= 4.0 s *t*= 6.0 s *t*= 8.0 s

Concentration distributions of tracers at different time by LES at N=6.67 s^{-1} (C=T/3,Q_G=1.67×10^{-4} m^3·s^{-1})

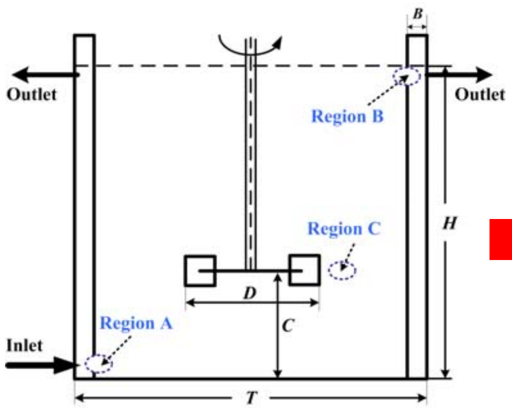


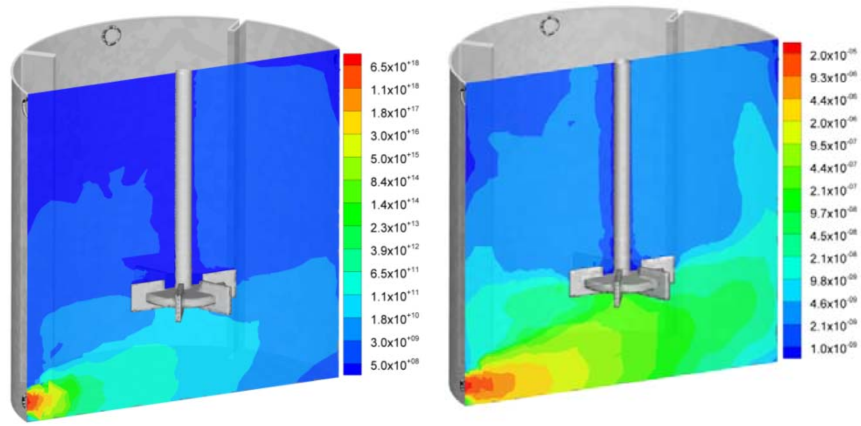
Effects of impeller speed and feed point on segregation index

Zhang et al., *Chem. Eng. Sci.*, 2009, 64, 2926-2933 (gas-liquid)
Zhao et al., *Ind. Eng. Chem. Res.*, 2011, 50, 5952-5958 (liquid-liquid)
Cheng et al., *Chem. Eng. Sci.*, 2012, 75: 256–266 (gas-liquid-liquid)
Feng et al., *Chem. Eng. Sci.*, 2012, 82, 272-284 (liquid-liquid flow)
Zhang et al., *Ind. Eng. Chem. Res.*, 2012, 51: 10124-10131 (gas-liquid)
Cheng et al., *Chem. Eng. Sci.*, 2012, 68, 469-480 (lqiuid-solid)
Yang et al., *Chem. Eng. Technol.*, 2013, 36, 443-449 (liquid-solid)
Cheng et al., *Chem. Eng. Sci.*, 2013, 101, 272-282 (liquid-liquid)

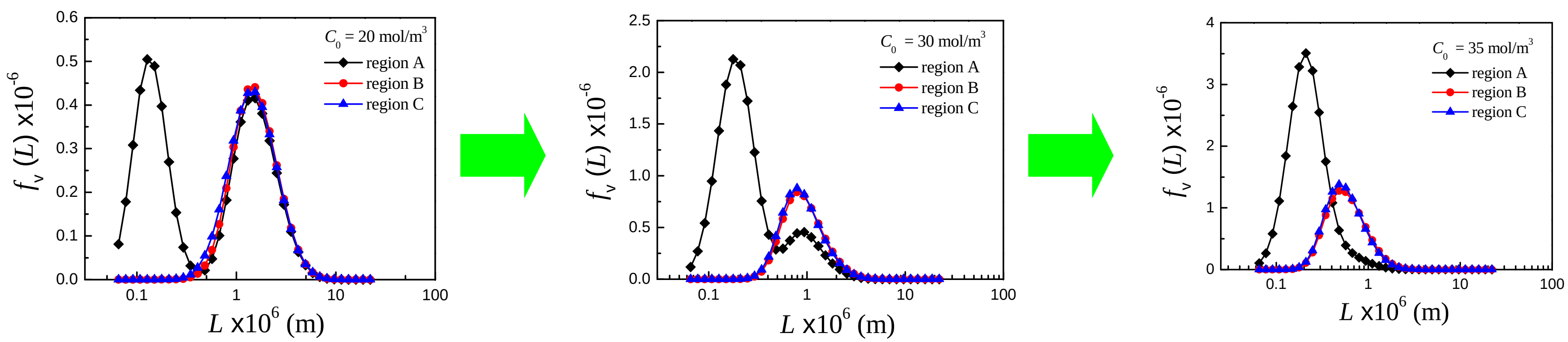
Simulation of a premixed precipitation process- multiclass CFD-PBE

Multimodal CSDs in certain locations and conditions are captured





Flow, mixing, transport and reaction with crystallization kinetics(nucleation, growth, aggregation and breakage)



CSDs of three investigated regions (A, B and C) at different inlet concentrations (t_R = 63 s, n = 372 rpm, with aggregation)

Cheng et al., *Chem. Eng. Sci.*, 2012, 68(1), 469-480
Cheng et al., *Ind. Eng. Chem. Res.*, 2009, 48: 6992-7003 **(high concentrations)**
Zhang et al., *Ind. Eng. Chem. Res.*, 2009, 48(1), 424–429 **(low concentrations)**

Application

Industrial Application of Simulation for Sustainability

more than 20 industrial reactors renovated (16 of SINOPEC)

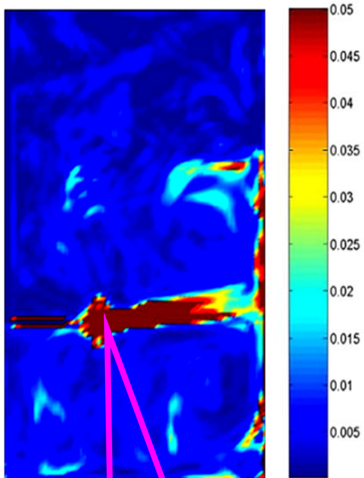
Four stirred reactors for hydrogenation of benzoic acid (each 40 m^3, gas-liquid-solid) economic benefit >10 million CNY/year

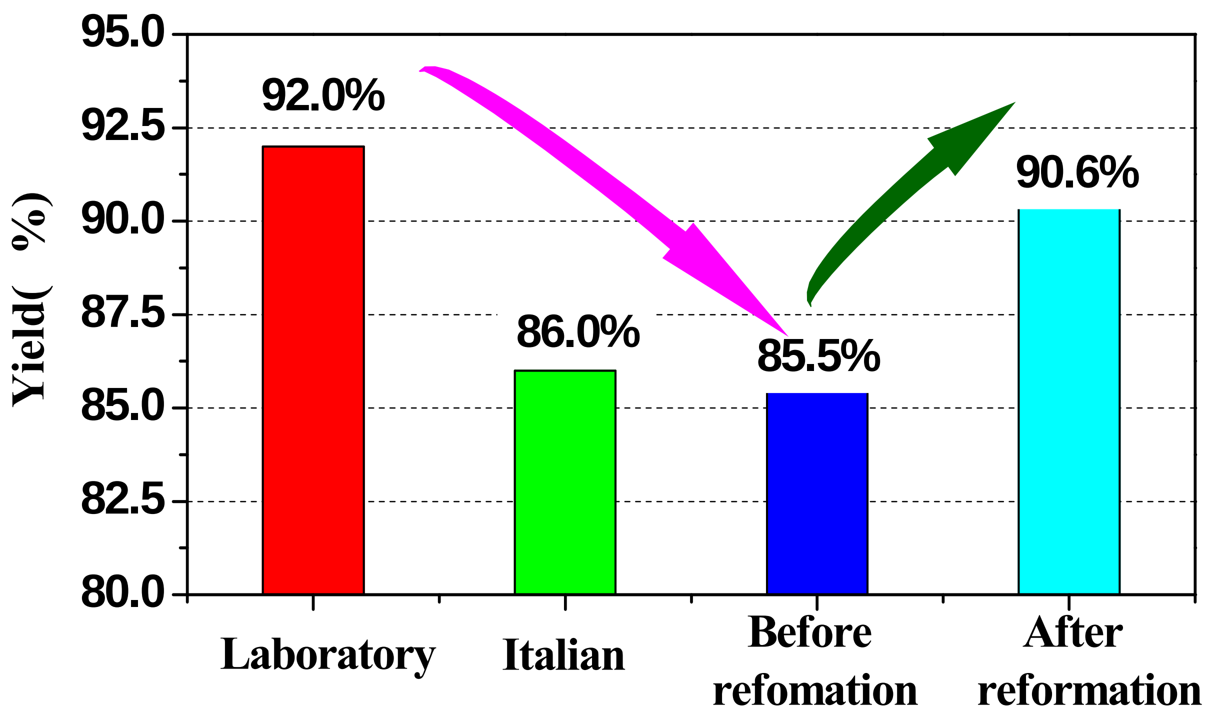
A reactor for toluene oxidation ($160m^3$, gas-liquid-solid) economic benefit > 6 million CNY/year

CFD tools: design, scale-up and optimization

Intensification of reactors for emission reduction & energy saving

Amidation reactors (9 G-L-L stirred tanks) intensified: overcome transport limitation





optimal mixing point (strongest energy dissipation)

New feeding point and new sparger: mixing is intensified, reaction yield raises by 5 percents, profits increase by about 90 millions CNY per year

SINOPEC [2008] No.74

Patent: ZL200810110439.4

Scale-up and optimization of industrial crystallizer

Caprolactam process scaled up from 50,000 ton per year to 160,000 ton per year (oil increased by 220%, H_2SO_4 increased by 30%)

Method 1： Swenson Co. in USA proposed that a new crystallizer must be built and investment is greater than 20 millions CNY.

Method 2： Based on models and in-house codes, IPE proposed to manipulate inner parts of crystallizer, and don't need a new one. Investment is less than 1 million CNY.

481m^3 crystallization reactor
(gas-liquid-liquid-solid, stirred＋loop)

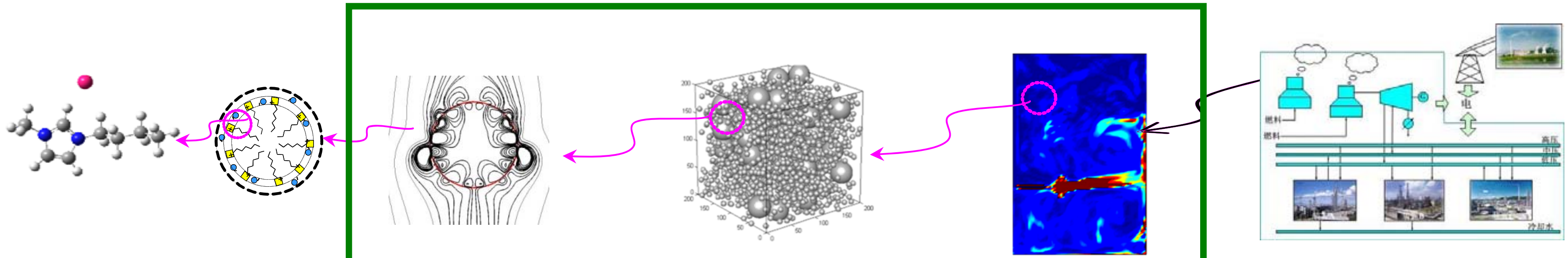
Patent: ZL 200910075440.2

IPE's proposal has been successfully used, 26 millions CNY investments are saved, 50 millions CNY per year profits are increased because of energy saving

SINOPEC [2010] NO.139

Perspective

Fundamental research of chemical engineering for sustainable industry is still significant



molecule **nano/micro** **bubble/drop/particle** **particle assemblage** **reactor** **plant**

10^{-12} m 10^{-9} m 10^{-6} m 10^{-3} m 10^{0} m 10^{3} m 10^{6}m

cooperate with chemists at nano/micro-scales

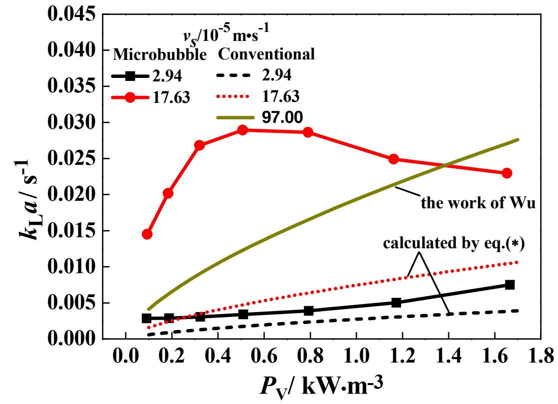
practical engineering models and numerical methods for industry

Design, scale-up and manipulation of multiphase reactors and crystallizers (Mixing, flow, transport and reaction)

Highly efficient reactors/crystallizers for sustainable industrial processes

(1) Intensify Transport at Interface:

$$N_A = k\,a\,(C_2 - C_1)$$



- **multiphase flow, mixing and transport at micro/nano-scales (microreactor, porous media, micro-electro-mechanical systems)**
- **microbubble, microemulsion, colloidal fluid (algal biofuels, sustainable energy)**

(2) scale-up of multiphase reactors and crystallizers

(to approach the yields at laboratory scales as closely as possible):

- **multi-scale models for multiphase transport and reaction in industrial reactors**
- **fast and accurate numerical methods for industrial reactors**
- **integrate the models and simulation into process systems engineering (process simulation, sustainable and ecological industry)**

Acknowledgements

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