Process Intensification and Green Chemistry

Process intensification

EPFL
Master of Science in Chemical Engineering and Biotechnology
Dr. H. Randall

Rev. 1 03/2023

Content

- Overview of Process Intensification (PI)
  - Definitions, illustrations, principles and benefits, classification of PI methods and equipment
- Selected examples of PI methodologies
  - Higee contactors
    - Overview
    - Rotating packed bed contactors
    - Rotating zigzag bed contactors
    - Two-stage counter-current rotating packed bed contactors
    - Characterization
    - Industrial applications
  - Spinning-disc reactors
    - Thin-film spinning-disk reactors
    - Rotor-stator spinning-disk reactors
  - Oscillatory baffled reactors / crystallizers
    - Fundamentals
    - Characterization and scaleup
    - Crystallization

1. Overview of Process Intensification

Process intensification (PI)

Early definition

- Established in the 1970s at ICI (goal was to reduce capital cost)
- Goal: to make dramatic reductions in plant volume (ideally 100 to 1000-fold)
    - ○ Compact design
    - ○ Hybrid unit
- Results:
    - ✓Improved intrinsic safety
    - ✓Reduced environmental impact
    - ✓Reduced energy consumption

PI: (one of the) current definition(s)

- Novel apparatus and techniques
- Drastic improvements in chemical manufacturing and processing
- Substantial reduction in either:
    - ○ Equipment size / production-capacity ratio
    - ○ Energy consumption
    - ○ Waste formation

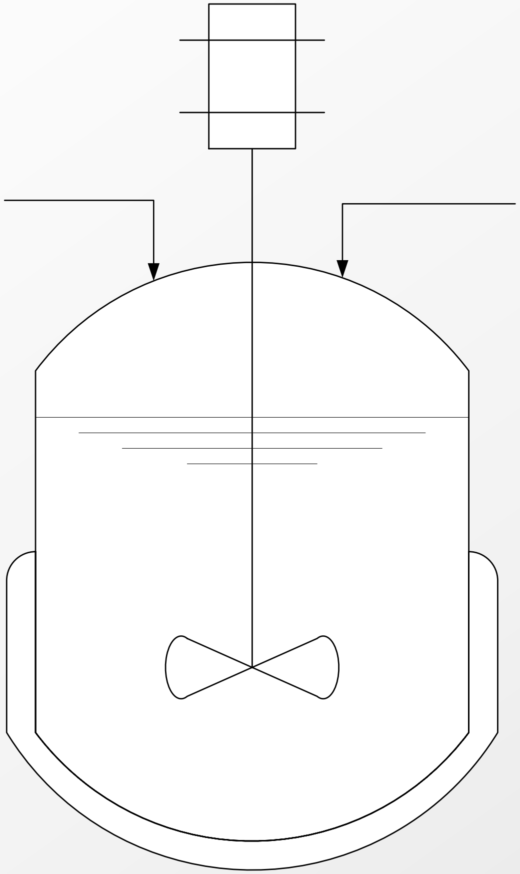
⇨Cheaper, safer, sustainable technologies

In short: any chemical engineering development leading to substantially smaller, cleaner and more energy-efficient technology

Stankiewicz, Chem. Eng. Prog. 96(1), 22-34 (2000)

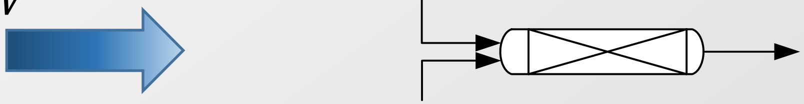
Illustration 1

- Batch to continuous
- Enhanced mass & heat transfer



Batch reactor

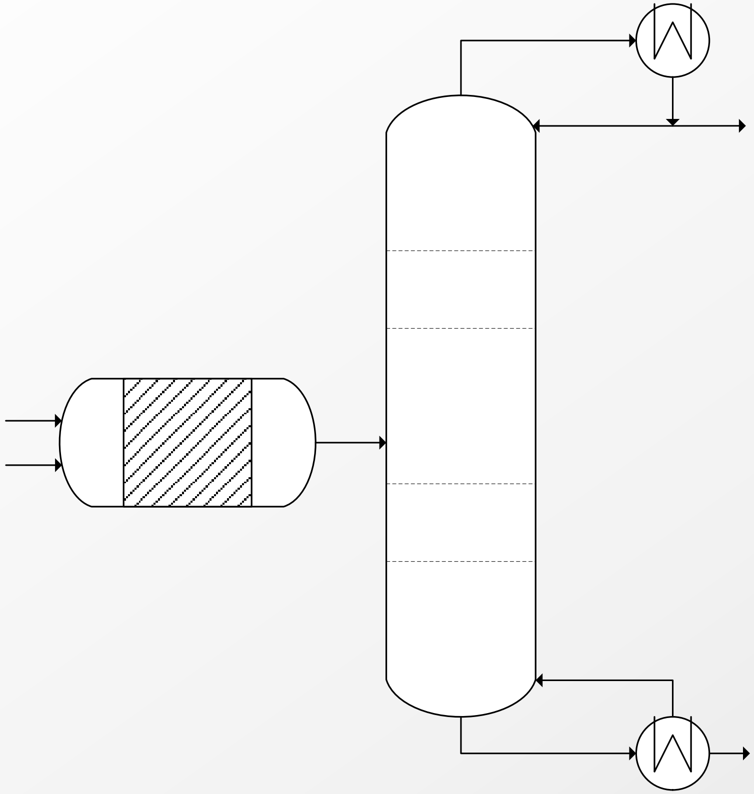
$$t_{mx}, U\frac{A}{V}, k_La, \sigma^2(\varepsilon), \sigma^2(\dot{\gamma})$$



Enhanced mixing/heating device

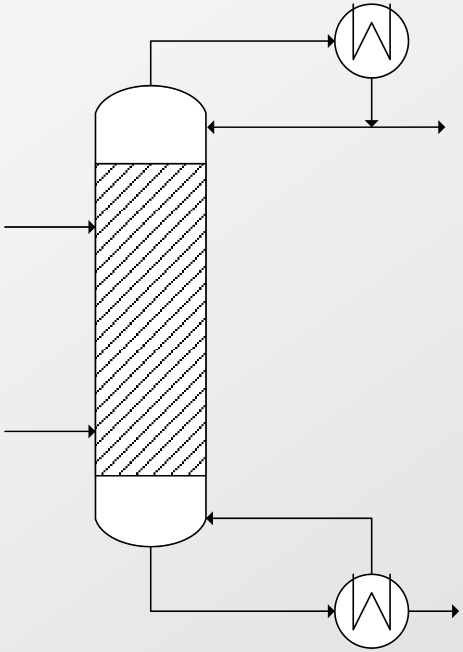
- Static-mixer reactor
- Micro-reactor
- Spinning-disk reactor
- Etc.

Illustration 2
Process integration



Reactor followed by distillation column

combine



Reactive distillation

Example: MTBE

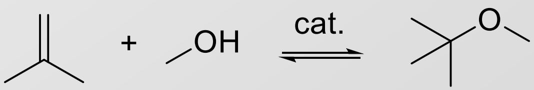
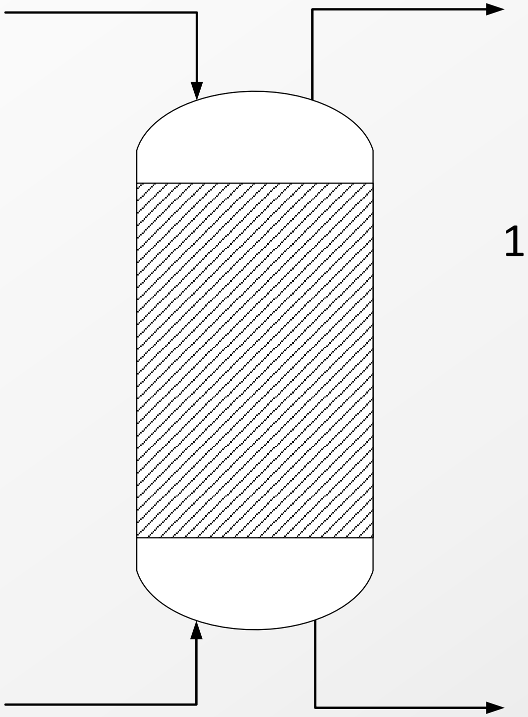


Illustration 3

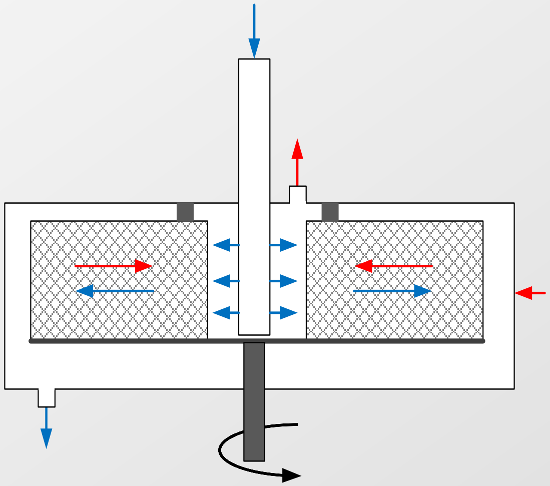
Gravity-enhanced mass transfer



Packed column

1 g → 100 – 1000 g

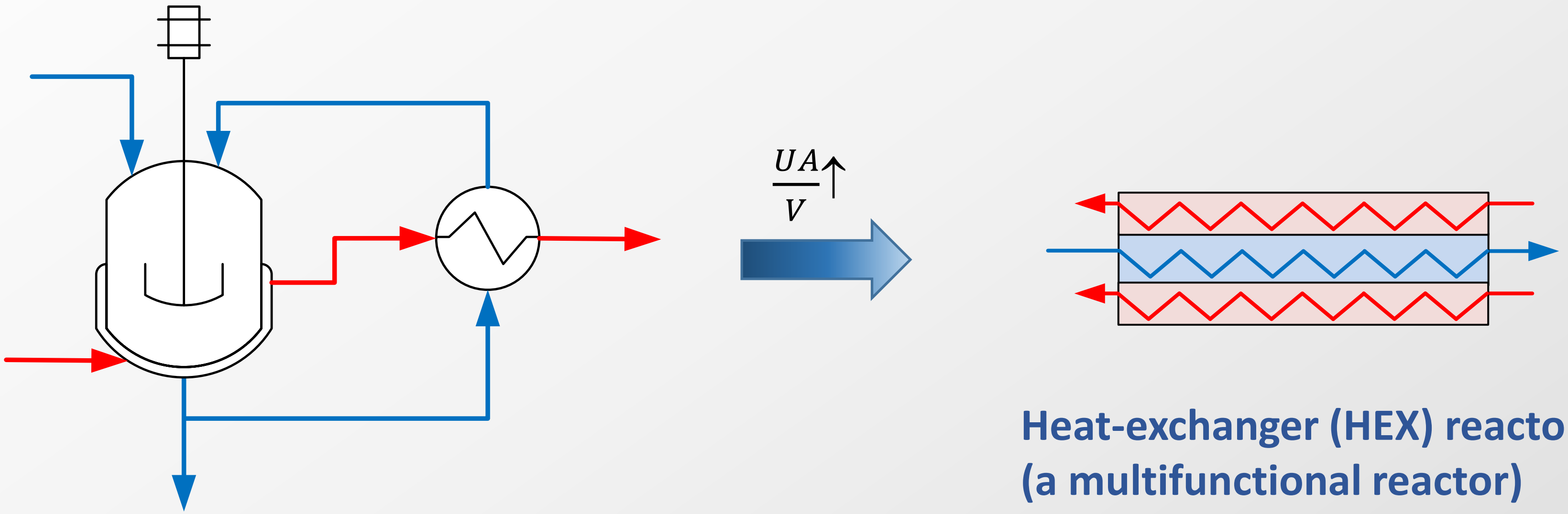
$t_{mx}, k_L a, HETP$



Rotating packed bed

Illustration 4

- Process integration
- Heat transfer enhancement

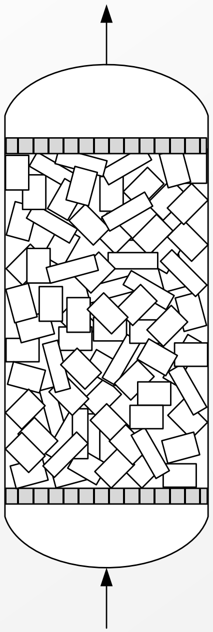


CSTR with heating jacket and external heat exchanger

Heat-exchanger (HEX) reactor (a multifunctional reactor)

Illustration 5

Mass and/or heat transfer enhancement



Fixed-bed reactor

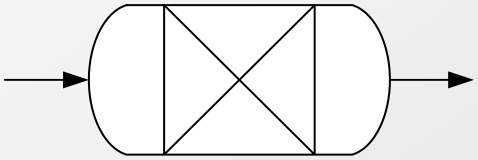
- Broad RTD
- External / internal mass / heat transfer limitations
- High pressure drop

$$Bo, \phi, \eta, \Omega, \Delta p$$

$$\phi = \sqrt{\frac{r(surf.\ rx.)}{r(int.\ diff.)}}$$

$$\eta = \frac{r(eff)}{r(T_{ext.\,surf}, c_{ext.\,surf})}$$

$$\Omega = \frac{r(eff)}{r(T_{bulk}, c_{bulk})}$$



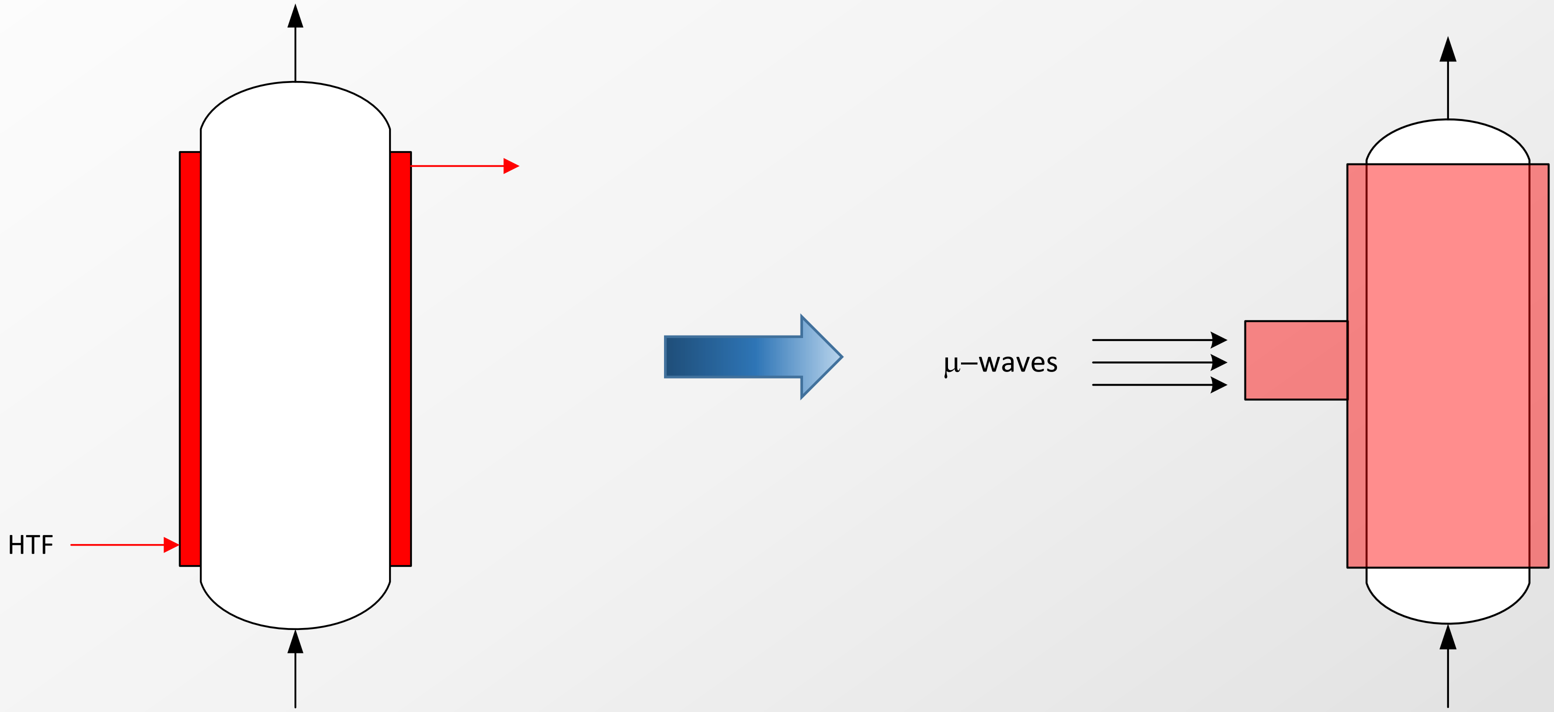
Structured catalyst reactor

- Catalytic foam
- Monoliths
- Gauze
- Impregnated static mixers
- etc.

- Narrow RTD
- Reduced mass transfer limitations
- Low pressure drop

Illustration 6

Enhanced heat transfer



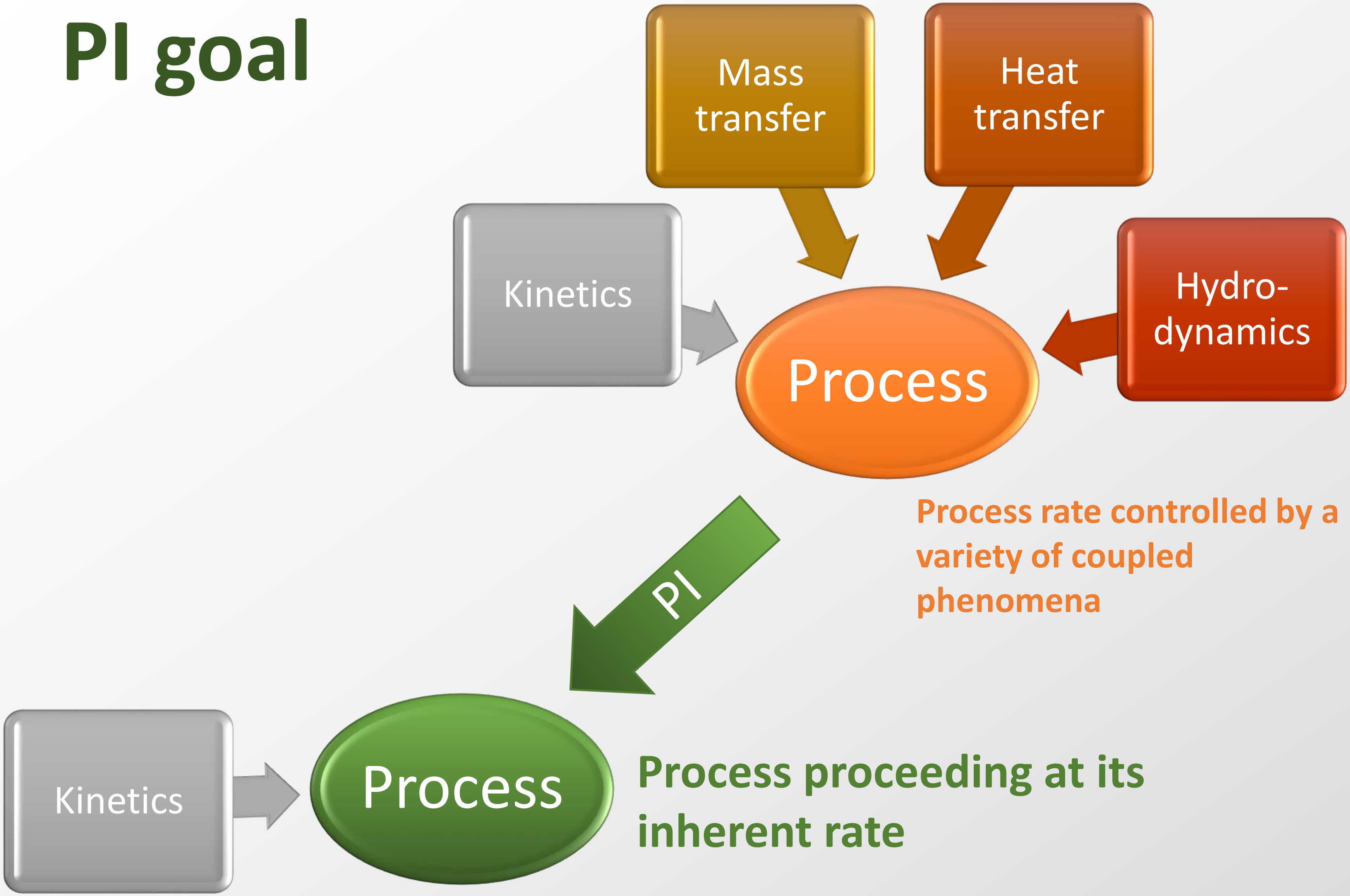
Tubular reactor with heating jacket

Conductive / convective heating

Microwave reactor

Direct heating
Selective heating possible

PI goal



Process rate controlled by a variety of coupled phenomena

Process proceeding at its inherent rate

Some of the benefits of PI

✓Lower energy consumption

✓Lower CO_2 emissions

✓Increased selectivity

✓Lower capital and operating costs

✓Increased safety

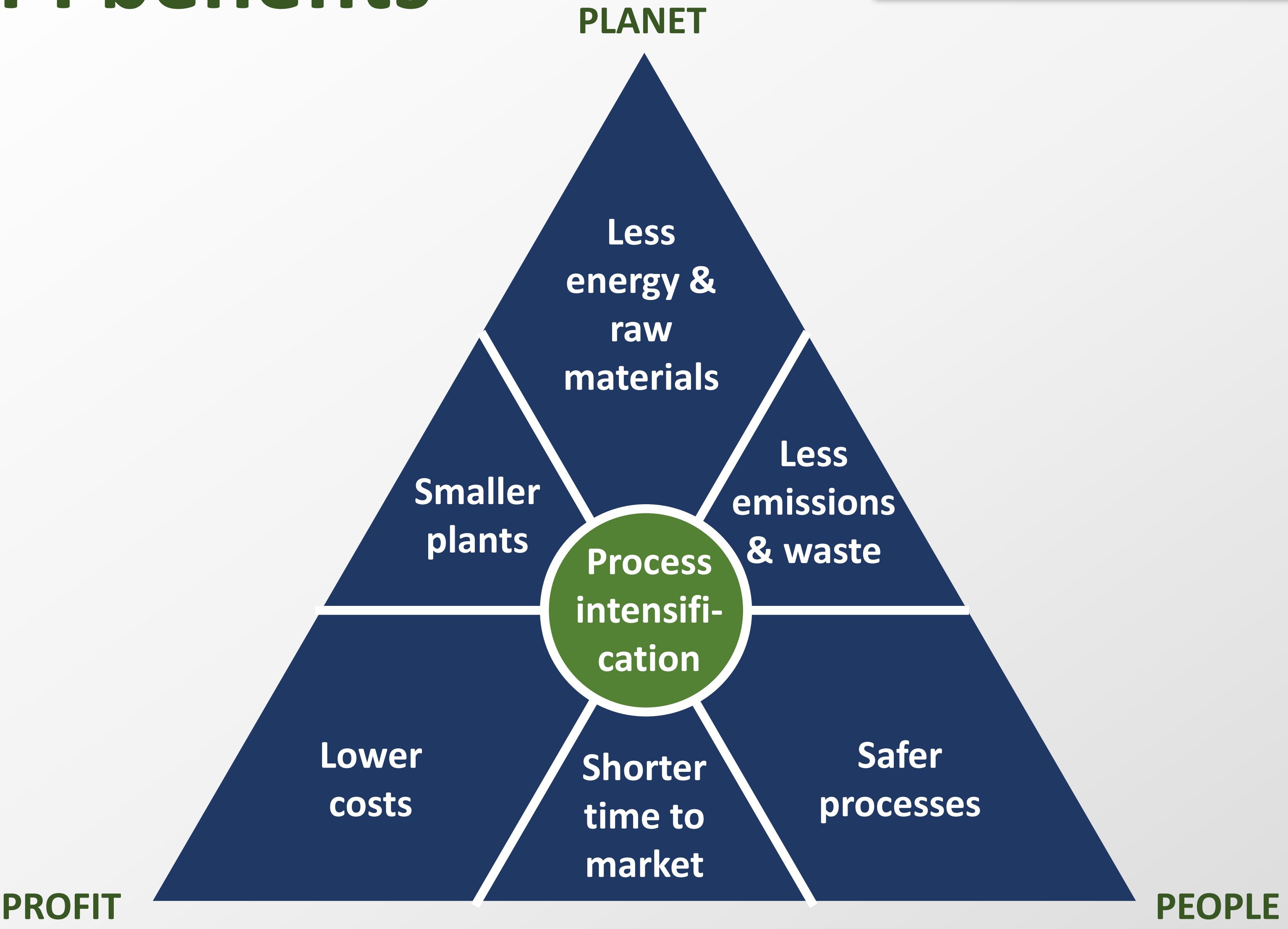
✓Reduced amounts of waste

✓Smaller process plants (positively affects social perception)

“Producing much more with much less”

PI benefits

PI → sustainable processes



Adapted from the European roadmap for process intensification, 2009

PI benefits by industrial sectors

Importance to sector	Pet. Chem.	Fine chem. & Pharma	Food ingredients	Consumer food
High	• Energy savings • Cost competitiveness • Safety • Regulation	• Selectivity • Cost competitiveness • Sustainability • Lead time	• Cost competitiveness[2]	• Cost competitiveness • Yield • Line availability • Product quality • Food safety • Product functionality
Medium	• Social impact • Reliability[1]	• Safety[1] • Reliability[1]	• Selectivity on end • Reliability on tolerances	• Energy savings • Plant safety • Flexibility
Low		• Energy savings	• Selectivity on waste streams	

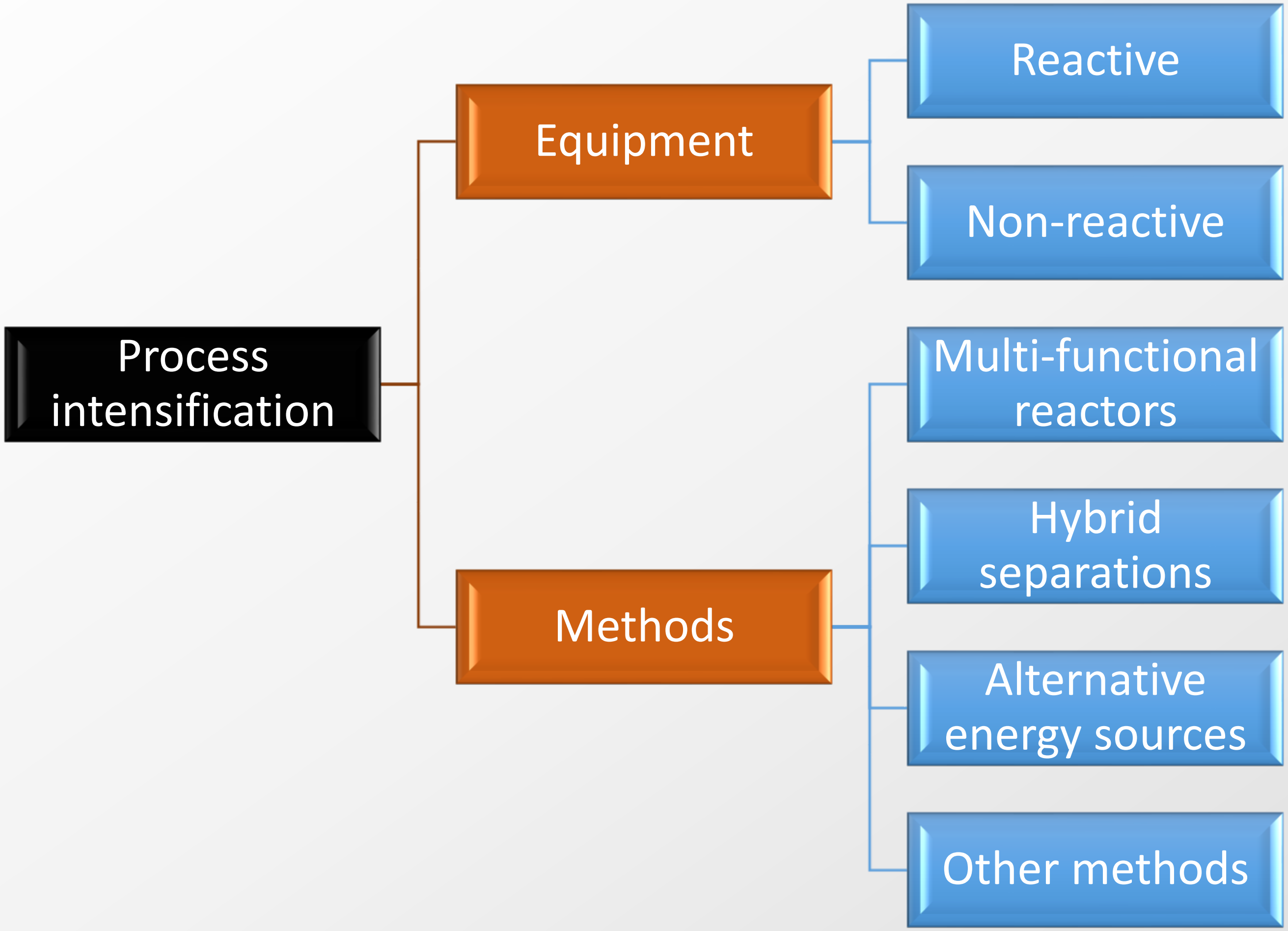
[1] Threshold requirement

[2] Driven by raw material and energy cost for processing

Three areas of chemical engineering: basic features

	Process optimization	**Process systems engineering**	**Process intensification**
Aim	Performance improvement of existing concepts	Multi-scale integration of existing and new concepts	Development of **new concepts** of process steps and equipment
Focus	Model Numerical method	Model Software	**Experiment**, **phenomenon**, **interphase**
Inter-disciplinarity	Weak (interface with applied mathematics)	Modest (applied mathematics, informatics, chemistry)	**Strong** (chemistry & catalysis, applied physics, mechanical engineering, materials science, electronics, etc.)

PI classification



- Process intensification
  - Equipment
    - Reactive
    - Non-reactive
  - Methods
    - Multi-functional reactors
    - Hybrid separations
    - Alternative energy sources
    - Other methods

One example:

Micro-reactors

Static mixers

Reactive extraction

Adsorptive distillation

Microwaves

Supercritical fluids

PI equipment (non-exhaustive)

Reactive

- Spinning disk reactor
- Rotor-stator spinning disk reactor
- Static mixer reactor
- Static mixing catalysts (Katapak)
- Monolithic reactors
- Micro-reactors
- Heat exchange reactors (HEX)
- Rotating packed-bed reactor
- COBR
- ATR

Non-reactive

- Static mixers
- Compact heat exchangers
- Micro heat exchangers
- Rotor/stator
- Rotating packed beds
- Centrifugal absorber
- Centrifugal extractors

PI methods (non-exhaustive)

Multi-functional reactors

- Reverse-flow reactors
- Reactive distillation
- Reactive extraction
- Reactive crystallization
- Reactive extrusion
- Membrane reactors
- Chromatographic reactors
- Heat integration

Hybrid separations

- Membrane absorption
- Membrane distillation
- Adsorptive distillation
- Extractive distillation
- Membrane extraction

PI methods (non-exhaustive)

Alternative energy sources

- Centrifugal fields
- Ultrasound
- Solar energy
- Microwaves
- Electric fields

Other methods

- Supercritical fluids
- Ionic liquids
- Dynamic/periodic reactor operation

PI general principles

- Maximize the effectiveness of intra- and intermolecular events
- Give each molecule the same processing experience
- Optimize the driving forces on every scale
  - Maximize the specific areas to which these driving forces apply
- Maximize synergetic effects from events and partial processes

Optional

Generic areas of PI

STRUCTURE

Spatial domain

- Molecular events
- Catalysts
- Phase contacting
- Transport phenomena

ENERGY

Thermodynamic domain

- Bringing energy to molecules
- Bringing energy to catalysts
- Energy transfer in hydrodynamics, mixing and transport phenomena
- Energy management in reactors and separation processes

SYNERGY

Functional domain

- Synergy on molecular scale
- Synergy in transport phenomena
- Synergy in processing units – multifunctional reactors and separation processes

TIME

Temporal domain

- Timing of events
- Applying dynamics
- Special process control

Generic areas of PI

Domain	Main focus	Examples of PI concepts
Spatial	Structured environment	Milli- and micro-channels Structured (catalyst) surfaces
Thermodynamic	Alternative forms and transfer mechanisms of energy	Electric and electromagnetic fields
Functional	Integration of functions/steps	Combination of alternative energy forms (e.g. electric and laser fields)
Temporal	Timing of events, introducing dynamics	Dynamic (pulsed) energy supply, milliseconds contacting

Barriers to implementation

- Insufficient PI knowledge and know-how
- No pilot facilities
- High technical & financial risk of developing first industrial prototype
- High technical & financial risk of implementation (retrofitting) of PI module in existing production lines(plants
- Insufficient awareness of potential benefits of PI technologies at the management level
- Process control systems not geared to control novel PI modules

2. Selected examples of PI technologies

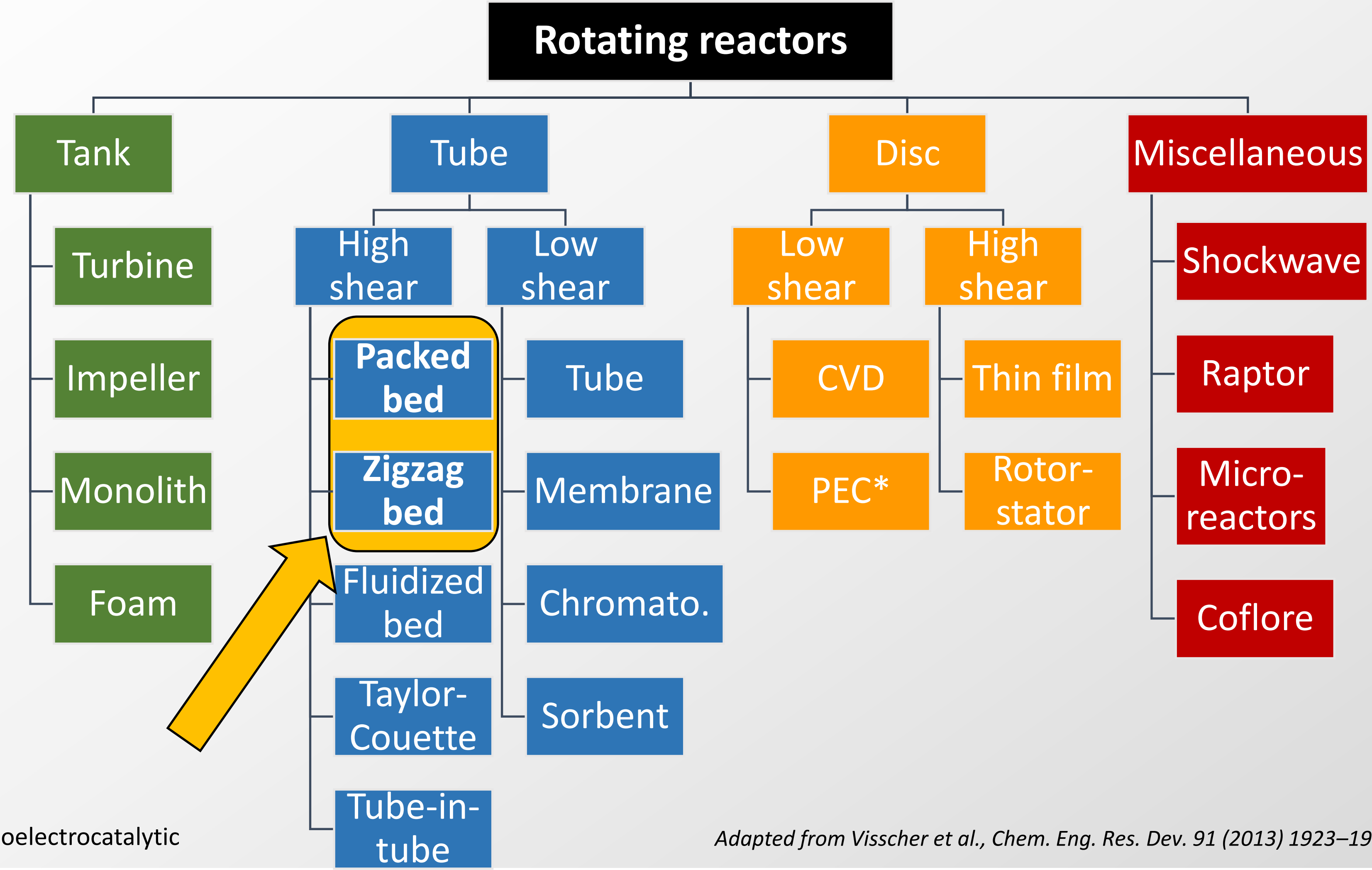
2.1. Higee contactors

2.1.1 Overview of Higee contactors

High-gravity ("Higee") rotating packed bed reactors

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

Classification of rotating reactors



Rotating reactors

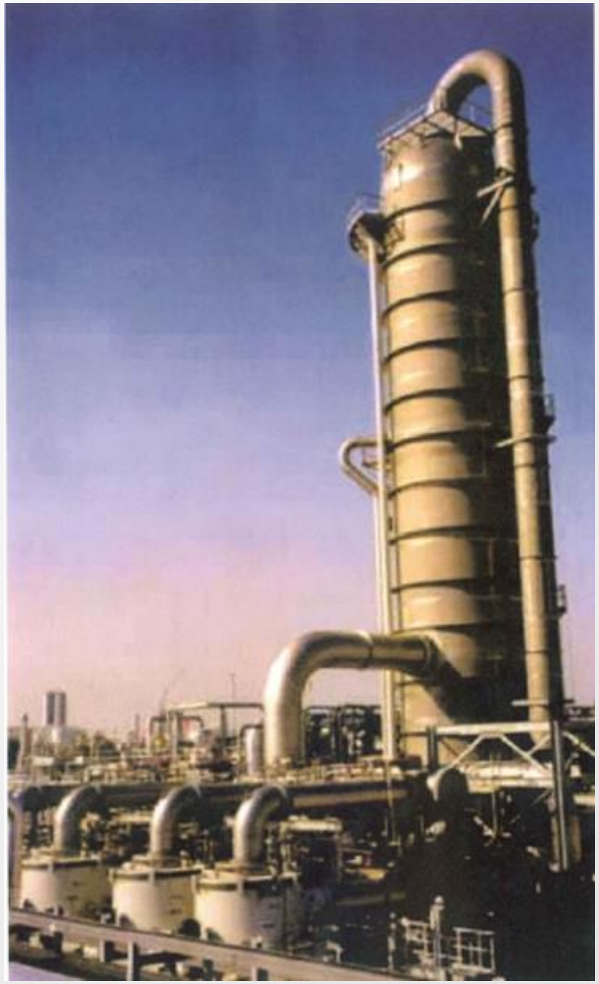
- Tank
  - Turbine
  - Impeller
  - Monolith
  - Foam
- Tube
  - High shear
    - **Packed bed**
    - **Zigzag bed**
    - Fluidized bed
    - Taylor-Couette
    - Tube-in-tube
  - Low shear
    - Tube
    - Membrane
    - Chromato.
    - Sorbent
- Disc
  - Low shear
    - CVD
    - PEC*
  - High shear
    - Thin film
    - Rotor-stator
- Miscellaneous
  - Shockwave
  - Raptor
  - Micro-reactors
  - Coflore

*Photoelectrocatalytic

Adapted from Visscher et al., Chem. Eng. Res. Dev. 91 (2013) 1923–1940

Rotating packed bed contactors for reactive stripping

HOCl process , Dow chemicals



Cl$_2$ absorption tower

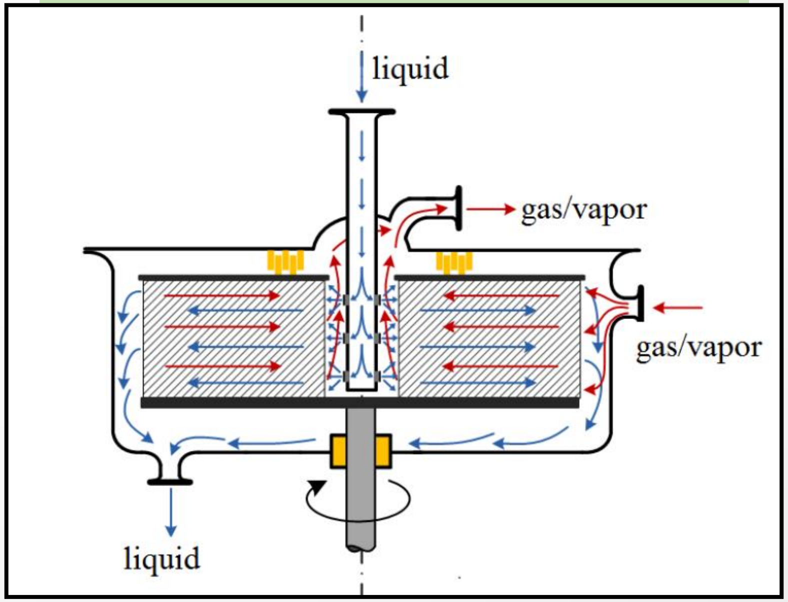
$$Cl_2(g) + NaOH(l) \rightarrow NaCl(l) + HOCl(l)$$

Rotating packed bed strippers

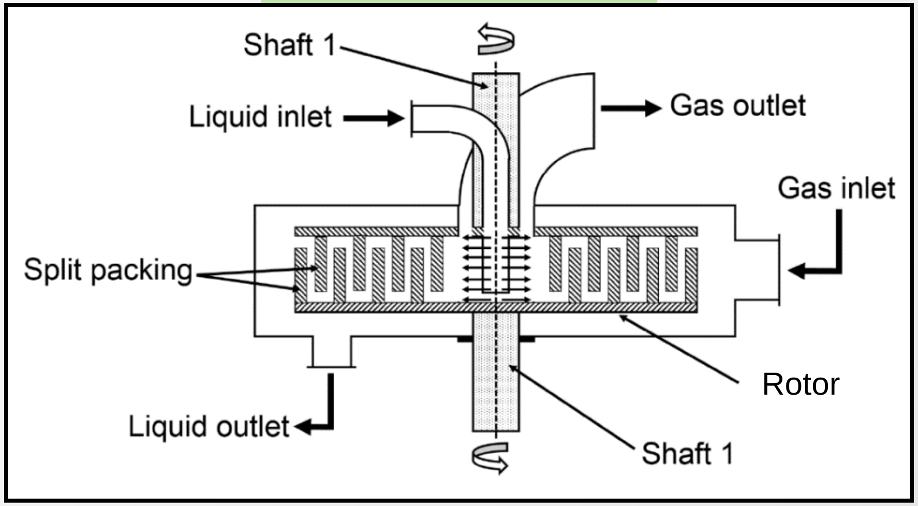
$$HOCl(l) \rightarrow HOCl(g)$$

Various Higee contactor configurations

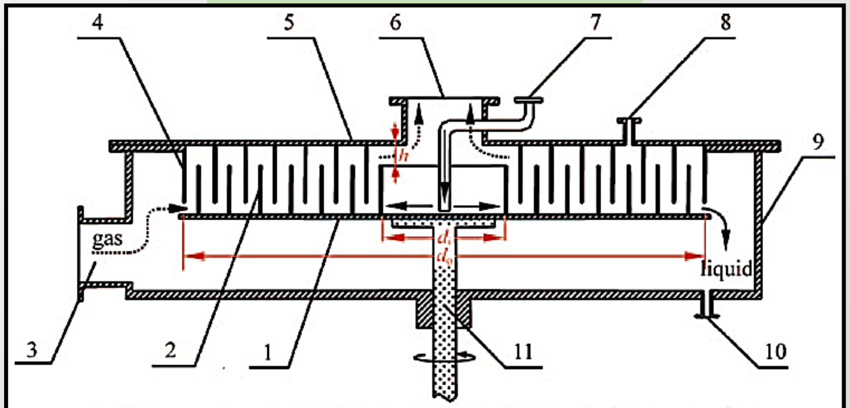
Single block, counter current RPB[1]



Split-packing RPB[1]



Rotating zigzag bed[2]



1-rotational disc 2-rotational baffle 3-gas inlet 4-stationary baffle 5-stationary disc 6-gas outlet 7-liquid inlet 8-Intermediate feed 9-liquid outlet 10-rotor casing 11-rotating shaft

[1] *Cortes Garcia et al., J Chem Technol Biotechnol* 2017; **92**: 1136–1156
[2] *Wang et al., Ind. Eng. Chem. Res., Vol. 47, No. 22, 2008*

Higee contactor features

- **High mass transfer rates**
  - ✓ High turbulence
  - ✓ Thin liquid films
- **High selectivity:**
  - ✓ Short contact time
- **Lower CAPEX and OPEX:**
  - ✓ Small footprint and height
  - ✓ Less material of construction (relevant for expensive materials, e.g., Hastelloy or Titanium)
  - ✓ Simple and quick start-up and shutdown procedures
- **New applications enabled:**
  - ✓ Processing of high-viscosity liquids
  - ✓ High-pressure operation
  - ✓ Mobile plants

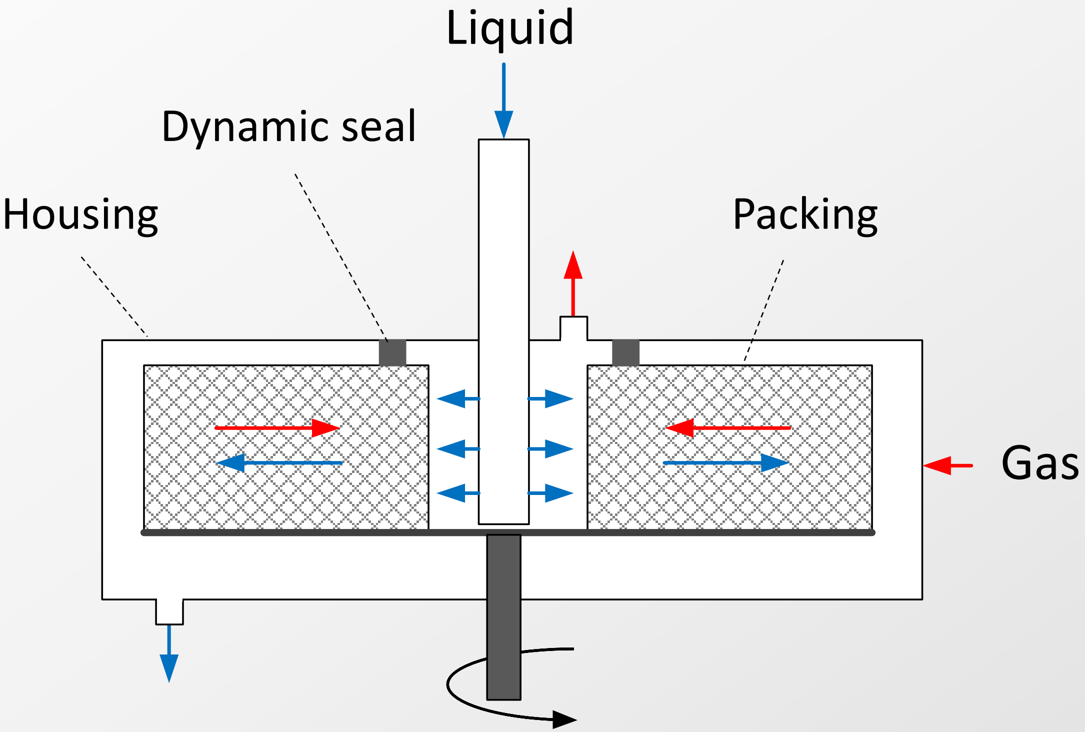
Higee contactors drawbacks

- Rotating equipment
- Additional energy requirements (electricity)
- Problems related to the reliability and longevity due to the moving parts
- Mechanical stability issues
- Complicated hydrodynamics
- Seals and bearings
- Higher pressure drop vs conventional packed beds
- No cooling/heating in bed

2.1. Higee contactors

2.1.2 Rotating packed bed (RPB) contactors

Countercurrent RPB arrangement



Potential flooding at center of rotor at high gas velocities

RPB principles

- Rotor = annular cylindrical packed bed
- Liquid fed at center (eye) of rotor
- Under the influence of centrifugal force (50-1000 g) liquid flows radially through the packed bed
- Liquid film, drops or spray formed as a result of multiple atomization
- Gas delivery options:
  - External zone of the rotor (i.e. counter-currently with liquid)
  - Bottom (i.e. cross-currently with liquid)

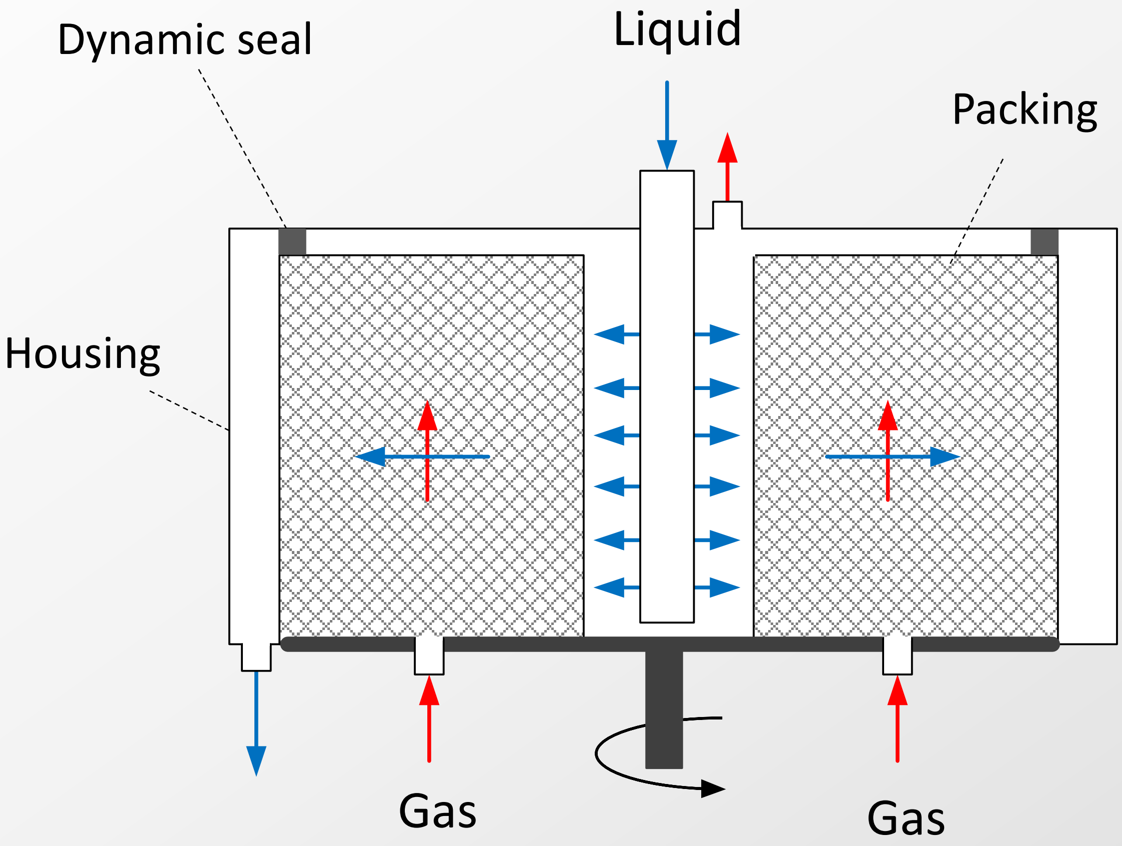
RPB features

- High mass transfer rates
  - Thinner films, smaller droplets → larger surface areas
- High g → increases flooding limits → operation at high gas velocities
- Low mixing times (~0.1 ms)
- Low HETP (1-2 cm)
- Broad RTD ($N_{CSTR} = 2$)
- Low liquid holdup (~5% of volume), which limits the mass transfer rate (compared to RZB)
- Packing can be made of various media (metal foam, wire mesh, corrugated sheet, …)

RPB features

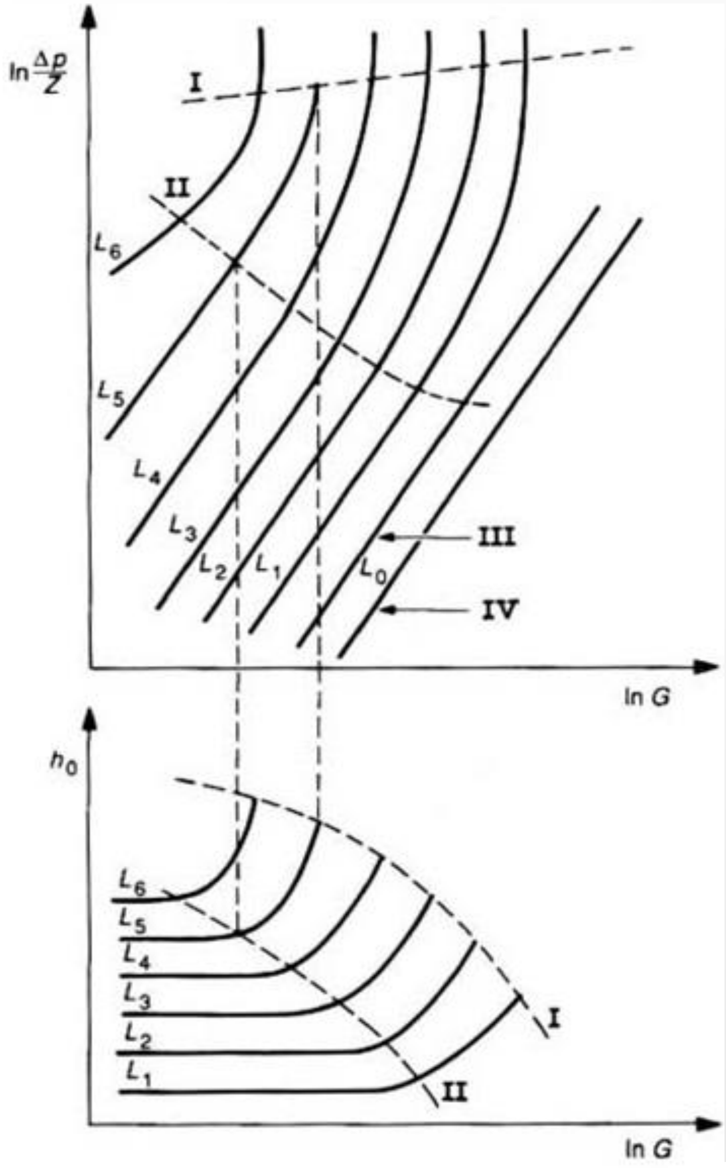
- Suitable for fast catalytic reactions (but low residence time of liquid phase due to low liquid holdup)
- Simple single block construction: higher mechanical strength than other rotors
- One additional degree of freedom for distillation : rotational speed
- Multiple rotors needed for continuous distillation because:
  - No middle feed-streams can be inserted
  - Limited amount of equilibrium stages
- Requires liquid distributors
- Applications: batch distillation, absorption, stripping, reaction, precipitation,…

Cross-current RPB arrangement



- ✓ Flooding limit extended since gas not removed at center of rotor
- ✓ Higher $k_L a$ and lower pressure drop than countercurrent

Reminder: pressure drop, dynamic holdup, flooding



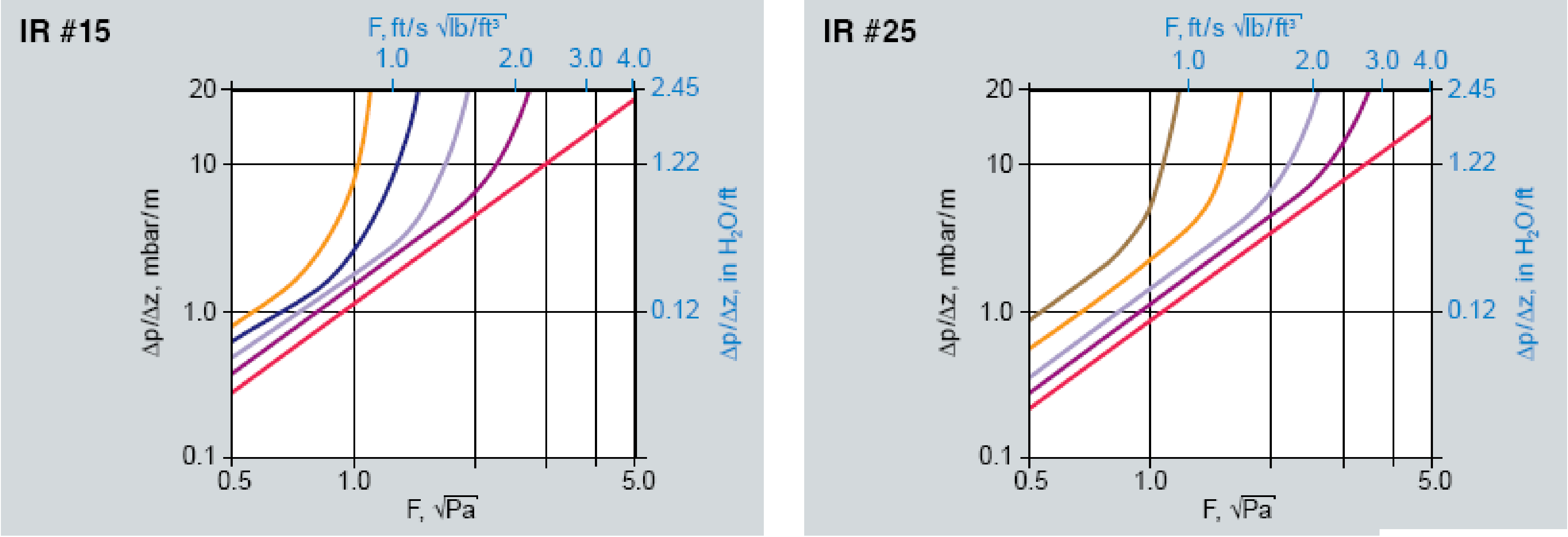
Variable	Description
$\frac{\Delta p}{Z}$	*Pressure drop per unit height*
G	*Gas mass velocity (mass time^{-1} area^{-1})*
L_0	*No liquid flowrate, i.e., no dynamic holdup (valid for III and IV)*
L_1 to L_6	*Increasing liquid mass velocity (mass time^{-1} area^{-1})*
h_0	*Dynamic holdup*
I	*Locus of flooding points*
II	*Locus of loading points*
III	*Wet, drained packing*
IV	*Dry packing*

Flooding occurs at excessive vapor flow:

- Liquid entrained upwards (friction)
- Increase in liquid holdup
- Sharp increase in pressure drop & decrease in separation efficiency

Random packing pressure drop

(ex: Sulzer Chemtech I-Ring)

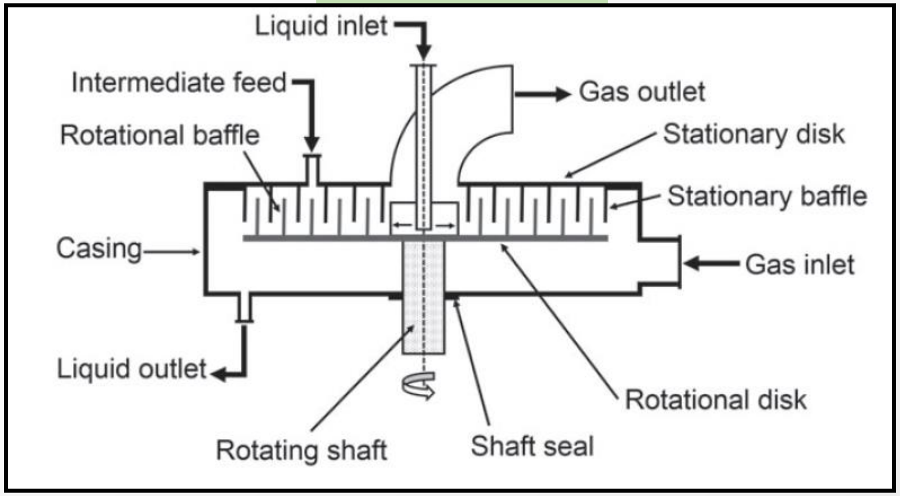


2.1 Higee contactors

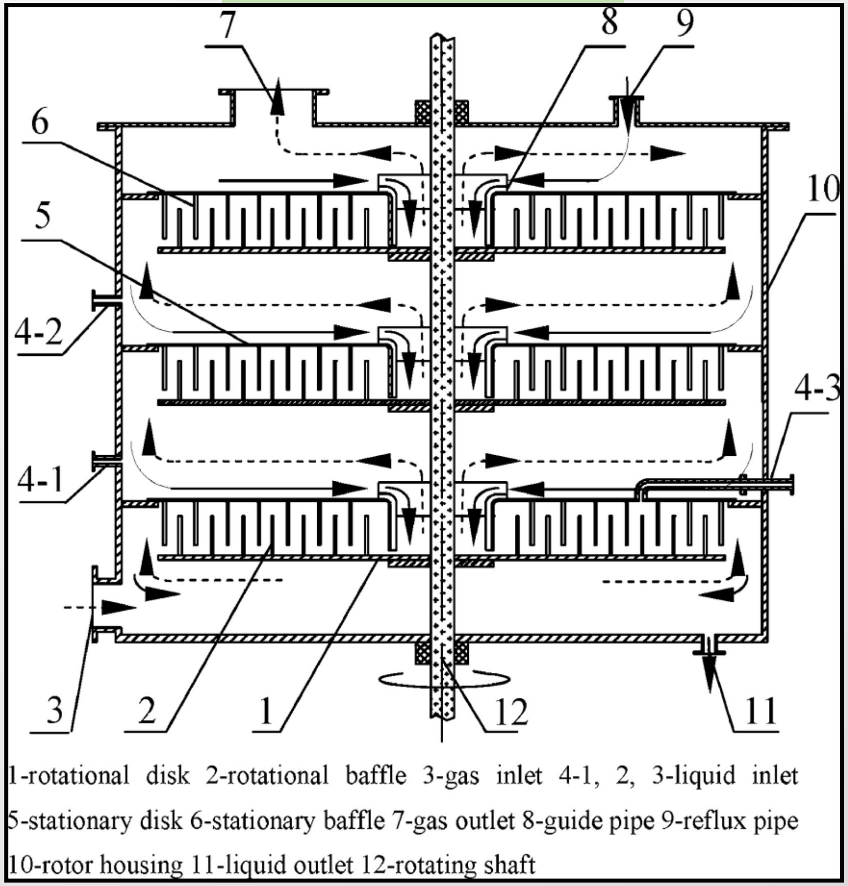
2.1.3 Rotating zigzag bed (RZB) contactors

Rotating zigzag bed (RZB)

Single rotor[1]



Multiple rotor[2]



[1] *Cortes Garcia et al., J Chem Technol Biotechnol* 2017; **92**: 1136–1156

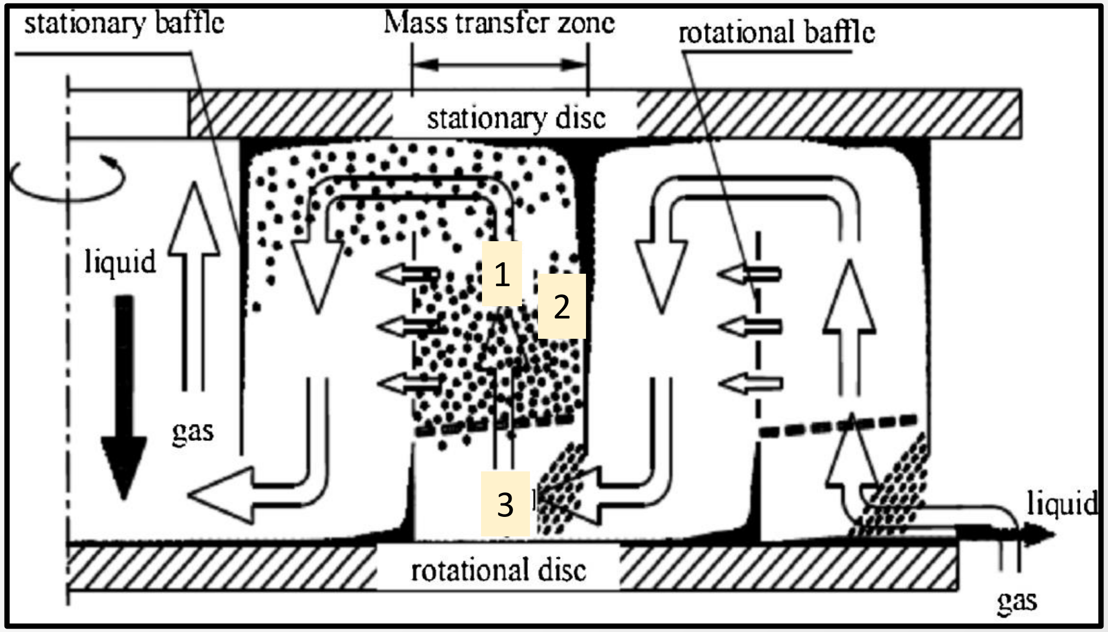
[2] *Wang et al., Chem. Eng. Res. Des. 89 (2011) 1434–1442*

Rotating zigzag bed (RZB) features

- One rotating disk and one stationary disk
- No packing (catalytic reactor not feasible)
- Concentric circular baffles on rotor and stator. Typically ~15mm between rings. Baffles on rotor are perforated.
- Operate typically above 500 g
- Volume divided by ~5 compared to RPB (larger diameter much lower height)
- Applications: batch or continuous distillation, absorption, stripping, reaction,…

Optional

Phase contacting mechanism in RZB



- Continuous gas phase flows in a staggered fashion and contacts with liquid phase
- Liquid phase repeatedly dispersed and coalesced
- Mass transfer zone:
  - Zone 1: crosscurrent contact of gas with liquid droplets
  - Zone 2: countercurrent gas contacting with liquid falling down stationary baffles
  - Zone 3: crosscurrent contact when liquid travels through space between stationary baffle and rotational disk

Wang et al., Chem. Eng. Res. Des. 89 (2011) 1434–1442

Optional

RZB comparison with RPB

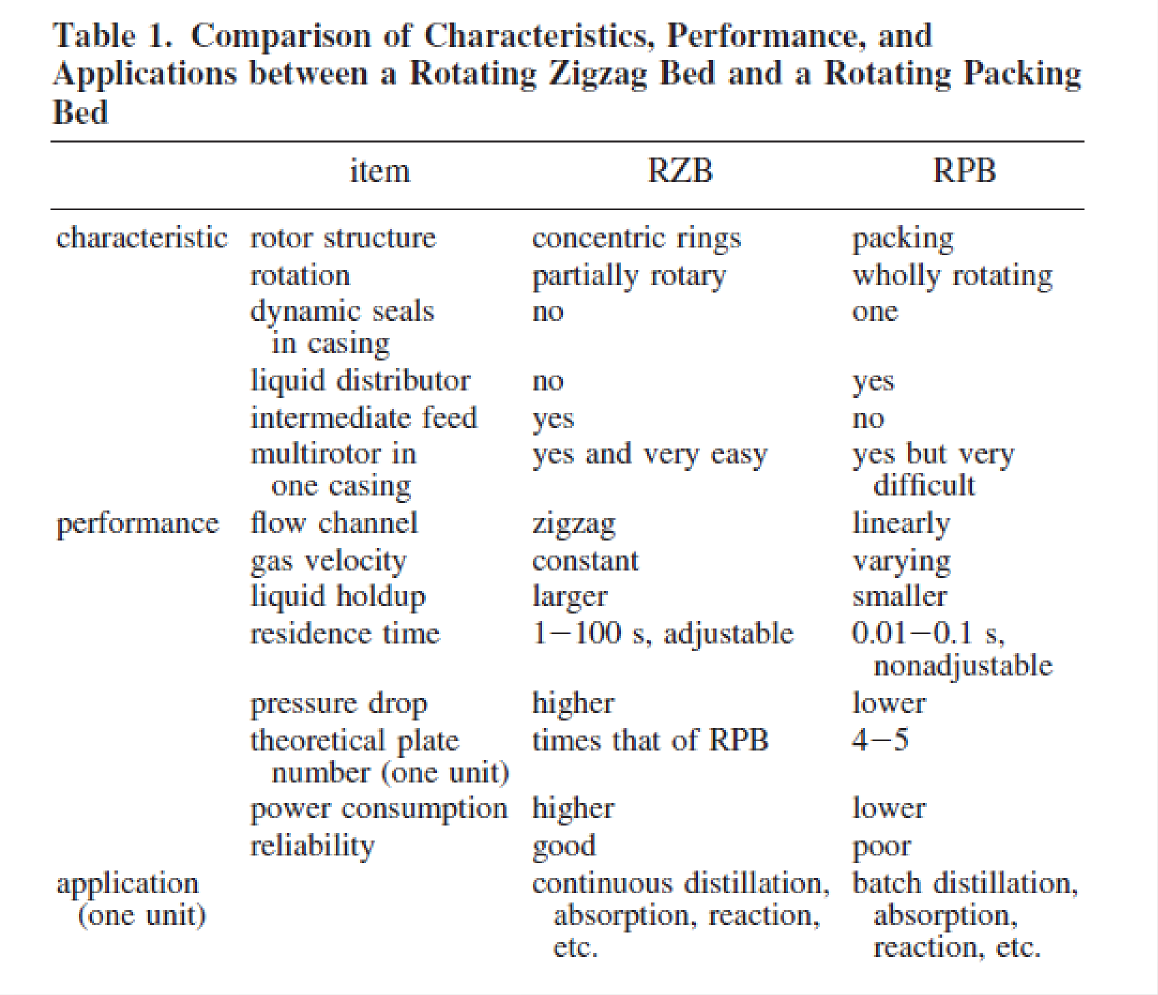


Table 1. Comparison of Characteristics, Performance, and Applications between a Rotating Zigzag Bed and a Rotating Packing Bed

	item	RZB	RPB
characteristic	rotor structure	concentric rings	packing
	rotation	partially rotary	wholly rotating
	dynamic seals in casing	no	one
	liquid distributor	no	yes
	intermediate feed	yes	no
	multirotor in one casing	yes and very easy	yes but very difficult
performance	flow channel	zigzag	linearly
	gas velocity	constant	varying
	liquid holdup	larger	smaller
	residence time	1−100 s, adjustable	0.01−0.1 s, nonadjustable
	pressure drop	higher	lower
	theoretical plate number (one unit)	times that of RPB	4−5
	power consumption	higher	lower
	reliability	good	poor
application (one unit)		continuous distillation, absorption, reaction, etc.	batch distillation, absorption, reaction, etc.

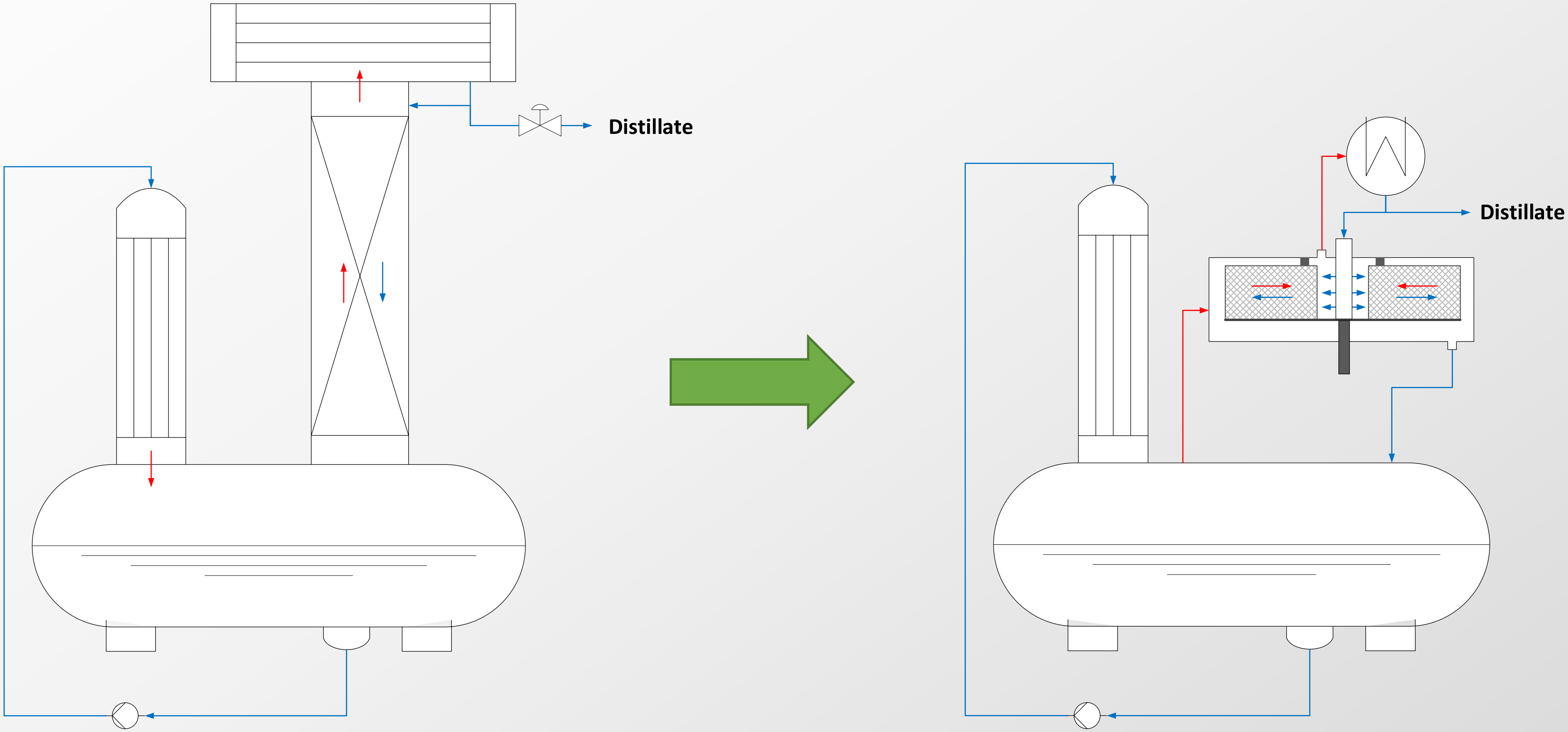
Wang et al., Ind. Eng. Chem. Res. 2008, 47, 8840–8846

RZB advantages over RPB

- No dynamic seal (only static seal)
- Can add feed inlets along separation path
- No liquid distributors needed
- High liquid holdup
- High & adjustable residence time of liquid phase (1-100 s). (RPB 0.01 - 0.1 s, nonadjustable.)
- Multiple RZB can be mounted on single shaft without dynamic seals
- Higher turndown ratio than RPB

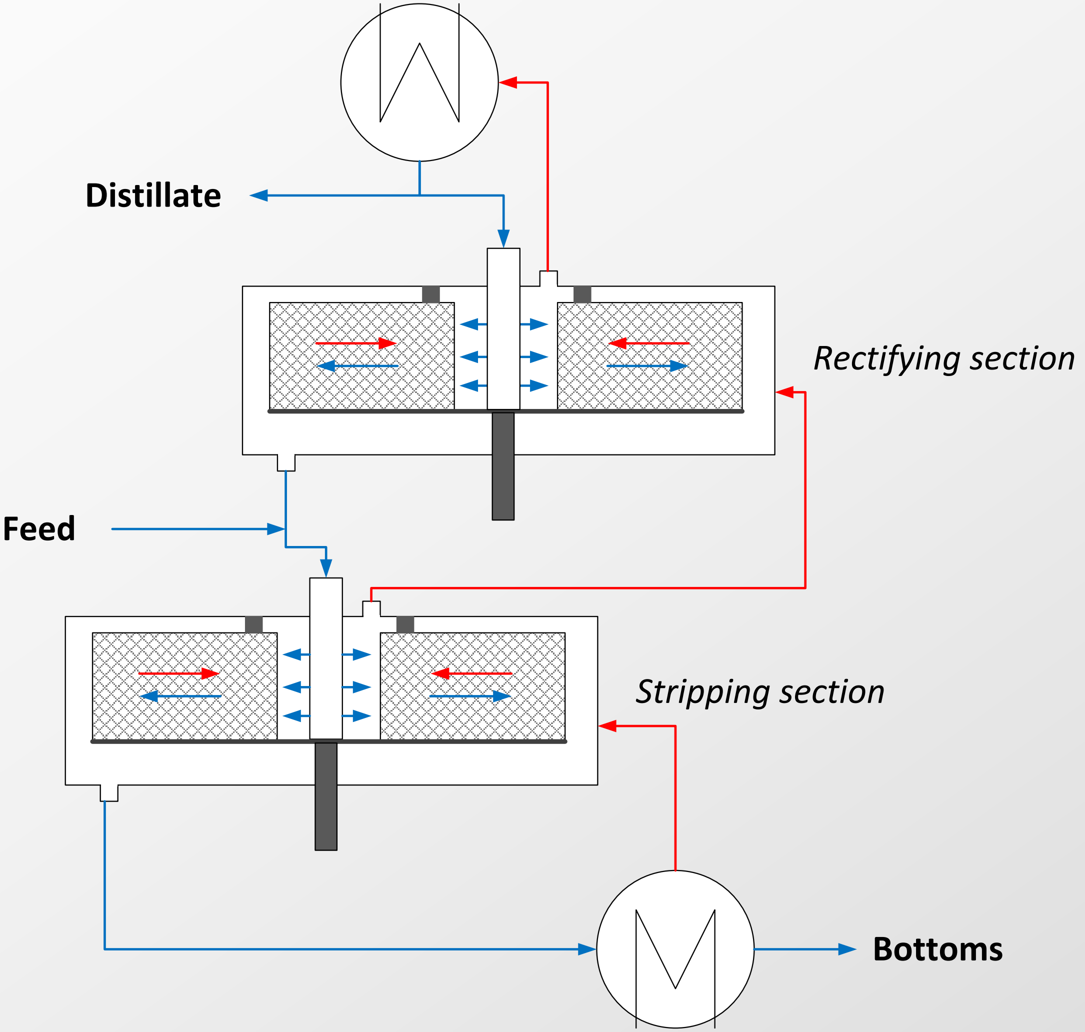
Higee vs conventional distillation

Batch configuration



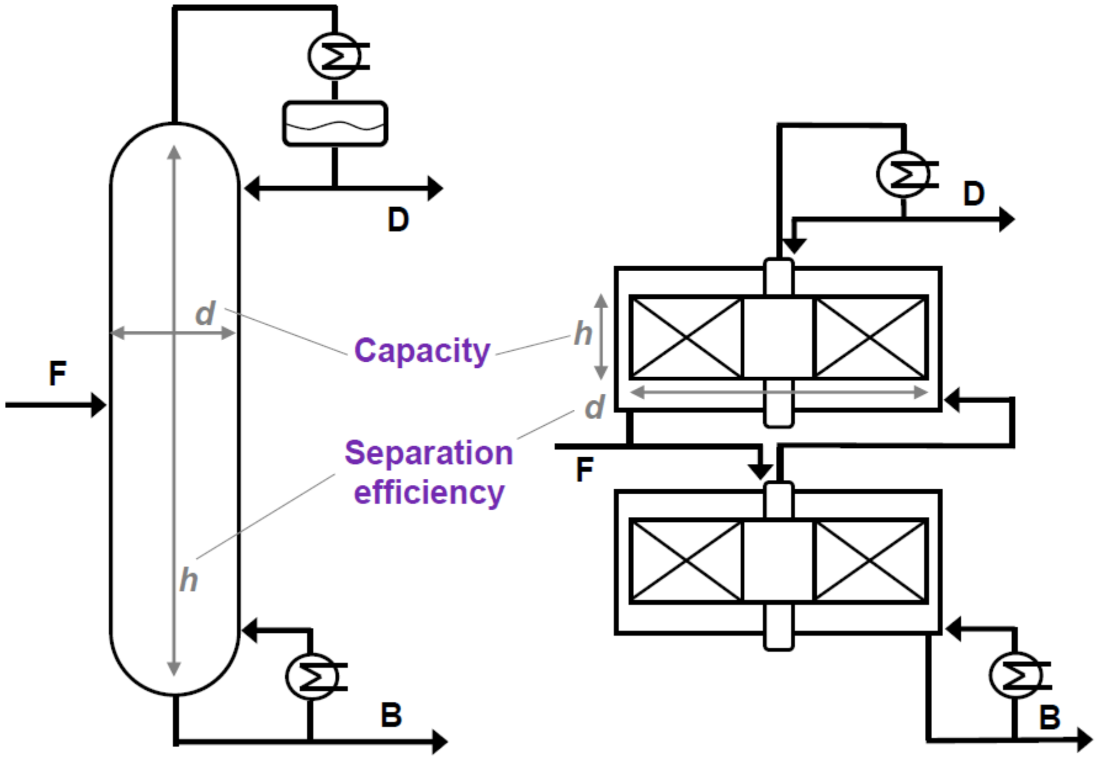
Higee vs conventional distillation

Continuous configuration



Higee vs conventional distillation

Continuous configuration



Garcia et al., J Chem Technol Biotechnol 2017; **92**: 1136–1156

Industrial RZB pictures

MeOH recovery unit

- Diam.=83 cm ; height=80 cm
- N=1000 rpm. Reflux ratio =1.5
- F=720 kg/h ; x_F = 70%
- x_D=99.8%, x_B=0.2%

EtOH recovery unit

- Diam.=80 cm ; height=55 cm
- N=1000 rpm. Reflux ratio = 2.5
- F=470 kg/h ; x_F = 45%
- x_D>95%, x_B<0.5%

Luo et al., Chemical Engineering and Processing 52 (2012) 55– 62

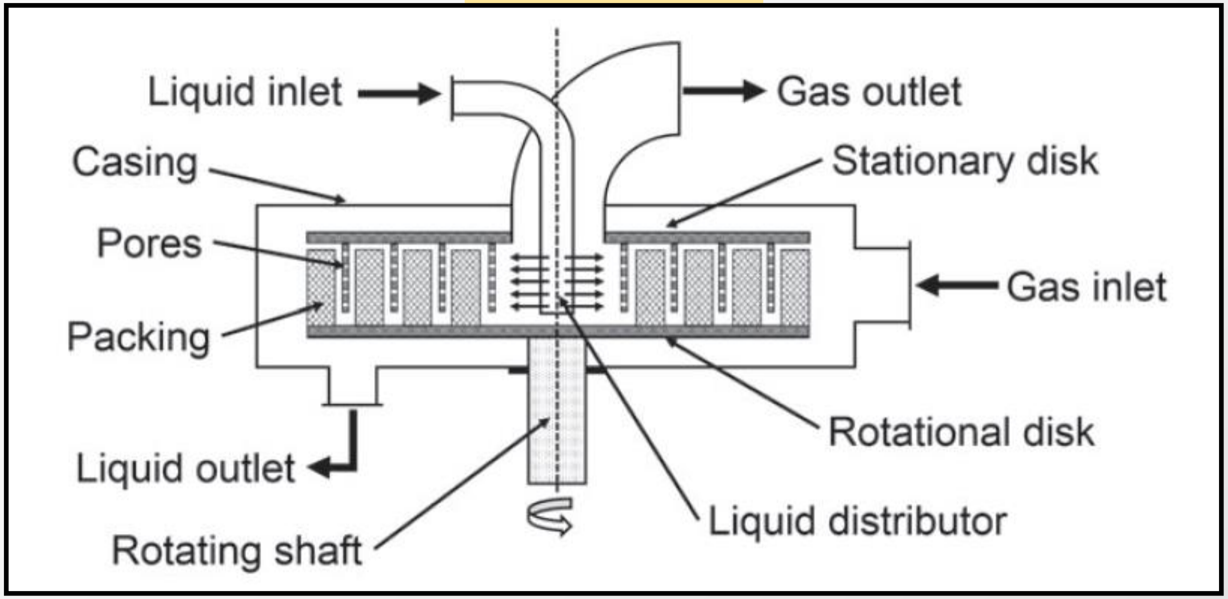
2.1 Higee contactors

2.1.4 Two-stage counter-current rotating packed bed (TSCC-RPB) contactors

TSCC-RPB scheme

Detail of single rotor

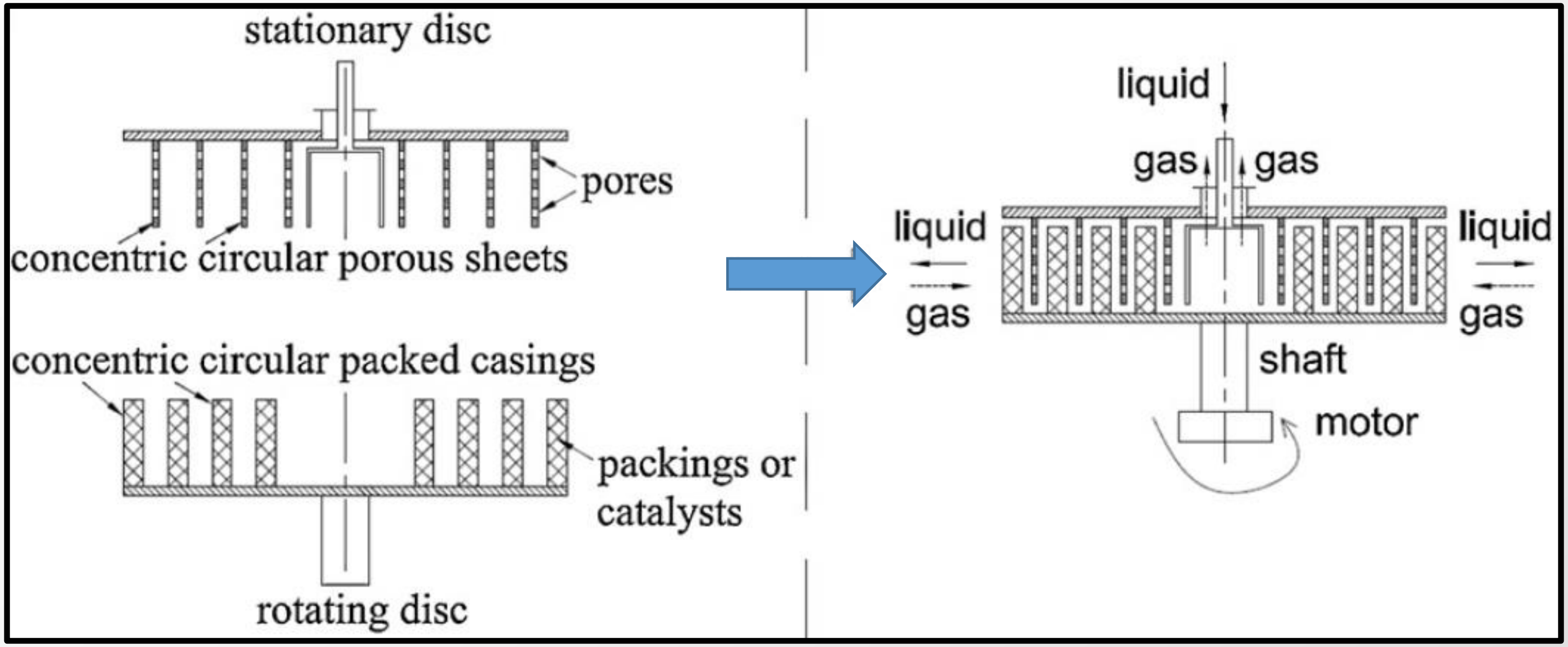
Single rotor



Cortes Garcia et al., J Chem Technol Biotechnol 2017; **92**: 1136–1156

TSCC-RPB

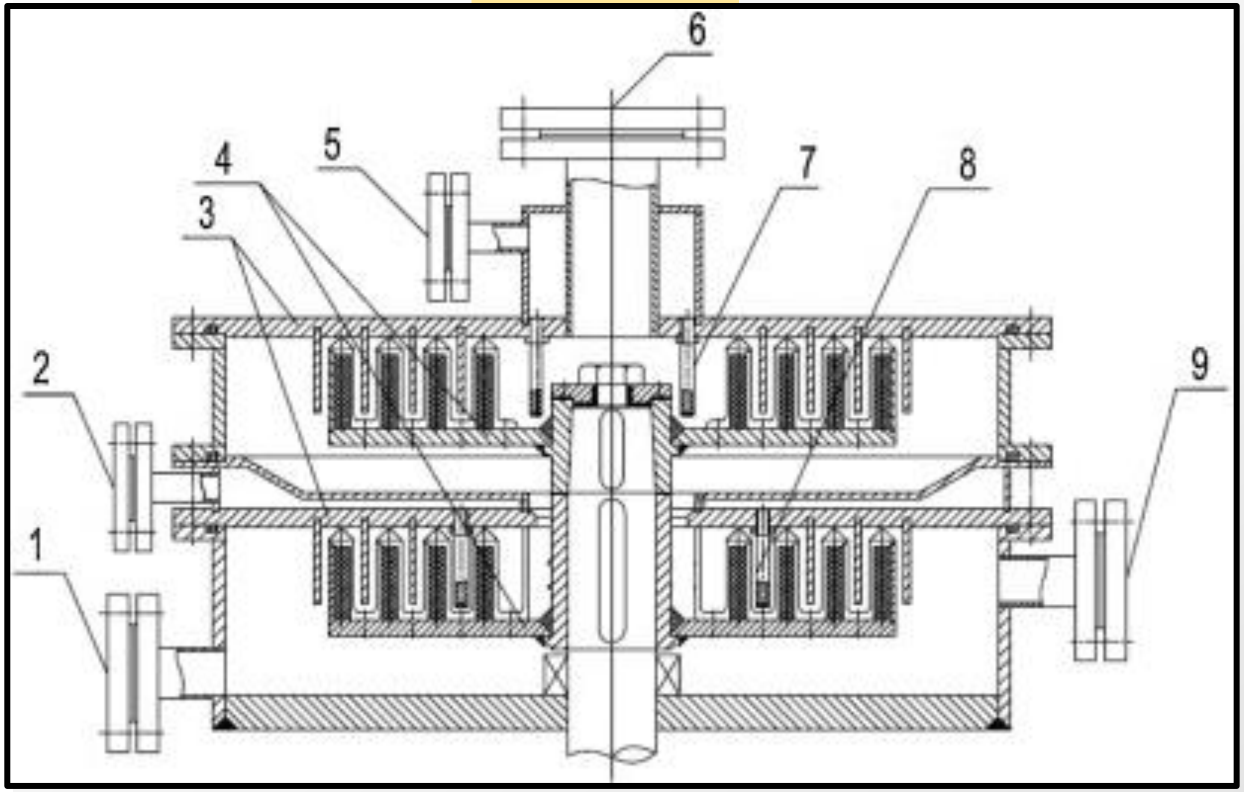
Detail of rotor



Y. Luo et al., Chemical Engineering and Processing *52 (2012) 55– 62*

TSCC-RPB scheme

Dual rotor

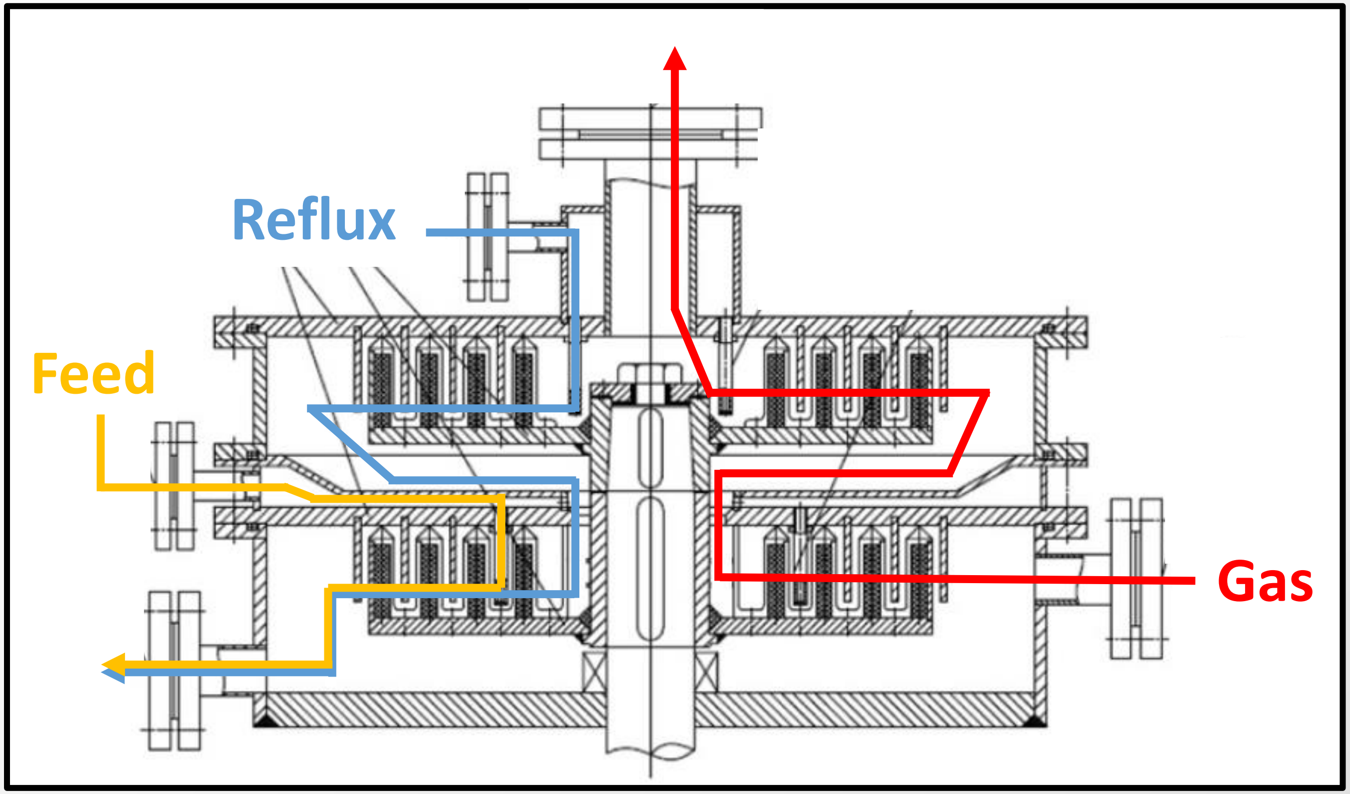


(1) liquid outlet
(2) liquid inlet 2 (intermediate feed)
(3) stationary disc
(4) rotational disc
(5) liquid inlet 1 (reflux feed)
(6) gas outlet
(7) liquid distributors
(8) liquid distributors
(9) gas inlet

Y. Luo et al., Chemical Engineering and Processing *52 (2012) 55– 62*

TSCC RPB scheme

Schematic gas and liquid flow trajectories

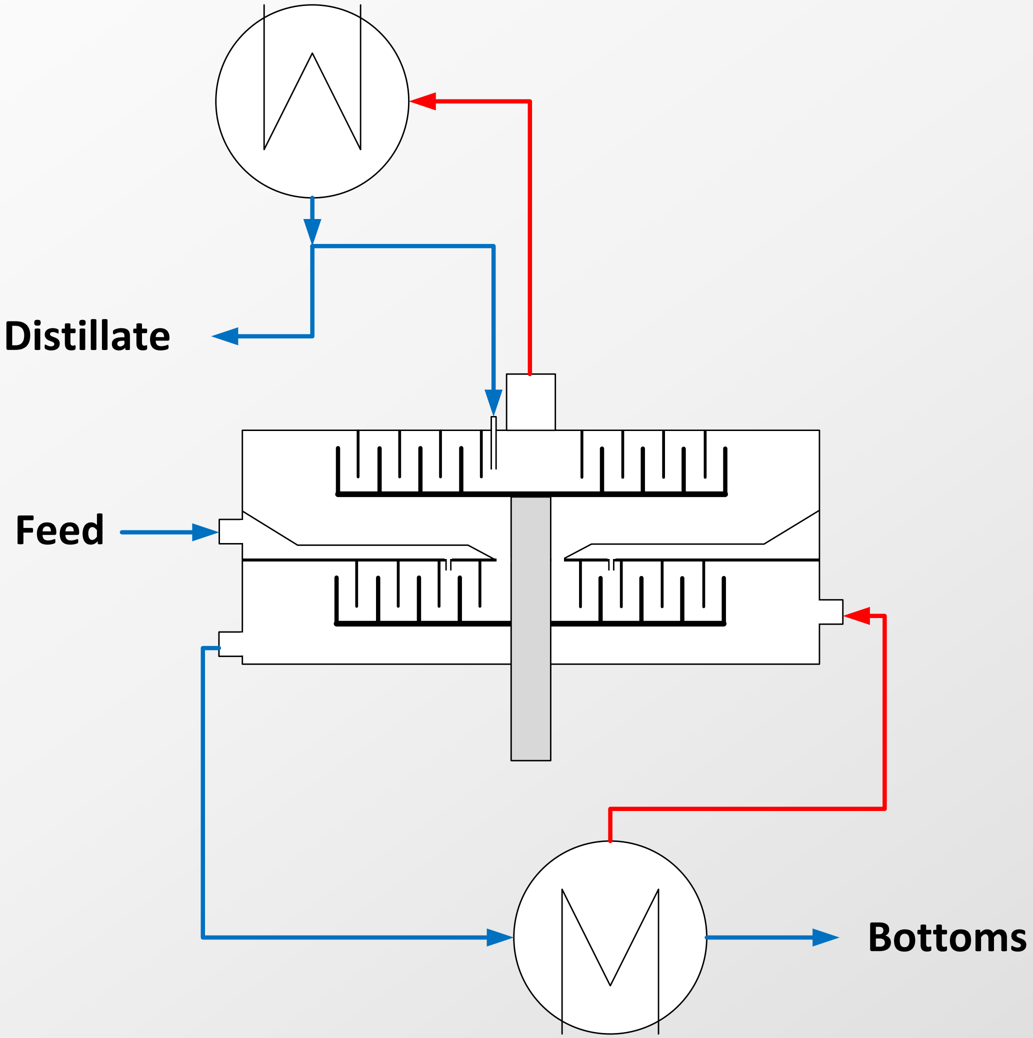


Adapted from Y. Luo et al., Chemical Engineering and Processing *52 (2012) 55– 62*

TSCC-RPB details

- Two rotors installed on single shaft
- Each rotor made up of rotating disk and stationary disk
- Packing rings attached to rotating disk & concentric rings attached to stationary disks to enhance liquid – packing collision and increase residence time
- Packing or catalyst may be included in packing rings for distillation, heterogeneously catalyzed reactions or (catalytic) reactive distillation
- Can be used for continuous distillation: upper rotor = rectifying section and lower rotor = stripping section.

Continuous distillation arrangement with TSCC RPB



Single rotor sufficient (two rotors needed with RPB)

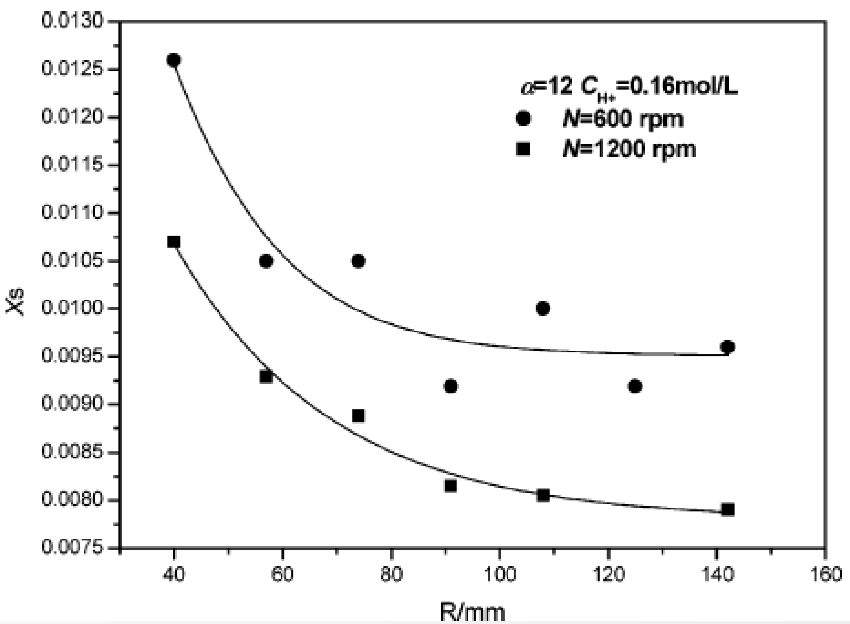
2.1 Higee contactors

2.1.5 Characterization of Higee contactors

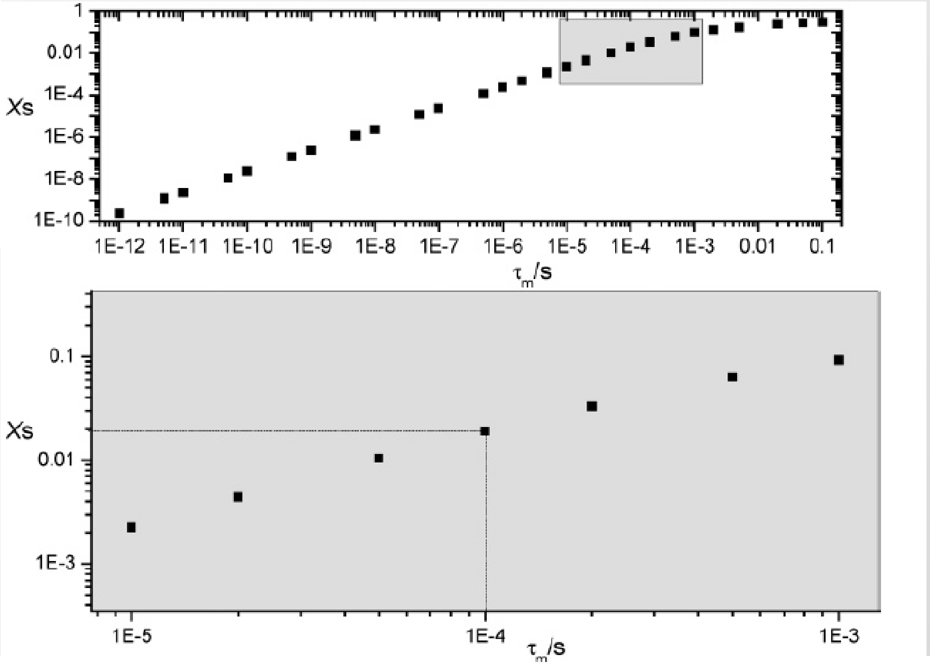
Typical measurements

- Mass transfer rate ($k_L a$)
- Micromixing time (τ_{mx})
- Residence time distribution (RTD, N_{CSTR} or Pe_{ax})
- $HETP$ and ATU
- Murphree efficiency (E_{MV} or E_{ML})

Segregation index & mixing time in RPB (see chapter 6)



$$\tau_{mx} < 0.1\, ms$$



$X_S = \frac{V_{CS}}{V_{CS}+V_{PM}}$ (segregation index)

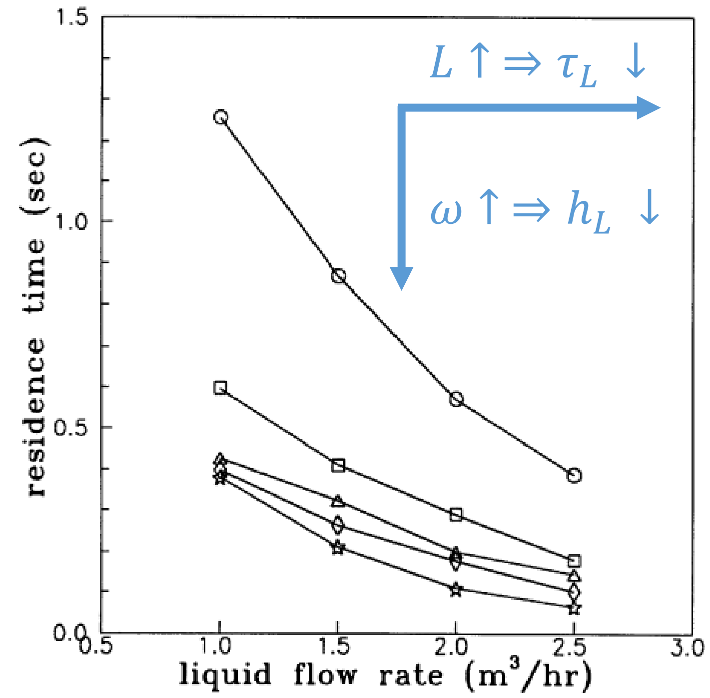
V_{PM}: Perfectly mixed volume

V_{CS}: Completely segregated volume

Yang et al., Ind. Eng. Chem. Res., Vol. 44, No. 20, 2005

Residence time in RPB

$$0.1\,s < \tau < 1\,s$$



$L \uparrow \Rightarrow \tau_L \downarrow$

$\omega \uparrow \Rightarrow h_L \downarrow$

Fig. 9. Residence time vs. liquid flow rate (foam metal). ($G = 0$, Rotating speed: ○ 400; □ 600; △800; ◇1000, ☆1200 rpm).

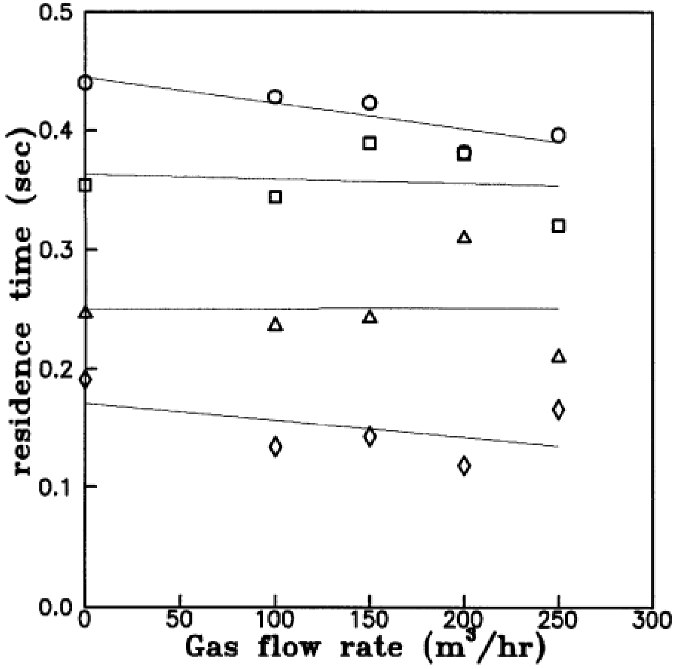
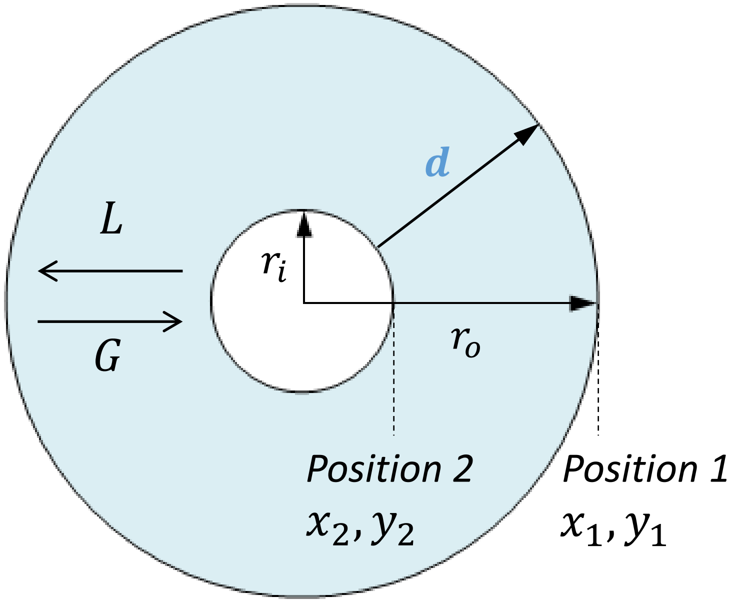


Fig. 10. Residence time vs. gas flow rate (wire mesh). (Point: experimental data, line: best fit; Rotating speed: ○□600; △◇ 1200 rpm; liquid flow rate: ○△ 1.5; □◇ 2.5 m^3/h).

Guo et al., Chemical Engineering Science 55 (2000) 1699-1706

RPB separation efficiency

Equilibrium-stage approach

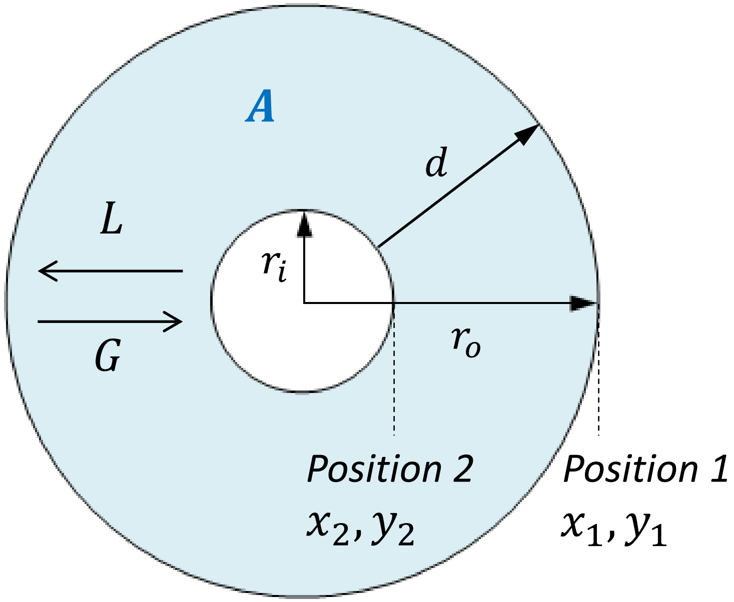


$$\boxed{HETP \times NTS = \boldsymbol{d}}$$

- $\boldsymbol{d} = r_o - r_i$: radial distance through packing $[m]$
- $HETP$: “height” equivalent to a theoretical plate $[m]$
  - Actually, a horizontal distance equivalent to a theoretical stage
  - Obtained from correlations or experimental data
- NTS: number of equilibrium stages
  - From equilibrium line and experimental outlet liquid and gas concentrations (graphically via Mc-Cabe Thiele or numerically)

RPB separation efficiency

Diffusional approach



$$\boxed{ATU \times NTU = \boldsymbol{A} = \pi({r_o}^2 - {r_i}^2)}$$

- $\boldsymbol{A}$: Area of the disk $[m^2]$
- ATU : Area of a transfer unit $[m^2]$
    - Obtained from correlations or experimental data
- NTU : Number of transfer units $[-]$
    - Experimentally determined from equilibrium line and experimental outlet liquid and gas concentrations by integrating the appropriate NTU equation (next slide)

RPB separation efficiency

Optional

Diffusional approach: concentrated cases

Individual gas film resistance

$$A = A_G \times N_G$$

$$A_G = \frac{G}{(r_o - r_i)\, k_G^0\, a\, p}$$

$$N_G = \int_{y_2}^{y_1} \frac{y_{BM}}{(1-y)(y-y_i)} dy$$

Individual liquid film resistance

$$A = A_L \times N_L$$

$$A_L = \frac{L}{(r_o - r_i)\, k_L^0\, a\overline{\rho_m}}$$

$$N_L = \int_{x_2}^{x_1} \frac{x_{BM}}{(1-x)(x_i - x)} dx$$

Overall gas film resistance

$$A = A_{OG} \times N_{OG}$$

$$A_{OG} = \frac{G}{(r_o - r_i)\, K_{OG}^0\, a\, p}$$

$$N_{OG} = \int_{y_2}^{y_1} \frac{y_{BM}^*}{(1-y)(y-y^*)} dy$$

Overall liquid film resistance

$$A = A_{OL} \times N_{OL}$$

$$A_{OL} = \frac{L}{(r_o - r_i)\, K_{OL}^0\, a\overline{\rho_m}}$$

$$N_{OL} = \int_{x_2}^{x_1} \frac{x_{BM}^*}{(1-x)(x^* - x)} dx$$

G and L in $mol \cdot s^{-1}$

RPB separation efficiency

Diffusional approach: dilute cases

Individual gas film resistance

$$A = A_G \times N_G$$

$$N_G = \int_{y_2}^{y_1} \frac{dy}{(y - y_i)}$$

Individual liquid film resistance

$$A = A_L \times N_L$$

$$N_L = \int_{x_2}^{x_1} \frac{dx}{(x_i - x)}$$

Numerical integration

Overall gas film resistance

$$A = A_{OG} \times N_{OG}$$

$$N_{OG} = \int_{y_2}^{y_1} \frac{dy}{(y - y^*)} = \frac{y_1 - y_2}{\overline{(y - y^*)}_{LM}}$$

Overall liquid film resistance

$$A = A_{OL} \times N_{OL}$$

$$N_{OL} = \int_{x_2}^{x_1} \frac{dx}{(x^* - x)} = \frac{x_1 - x_2}{\overline{(x^* - x)}_{LM}}$$

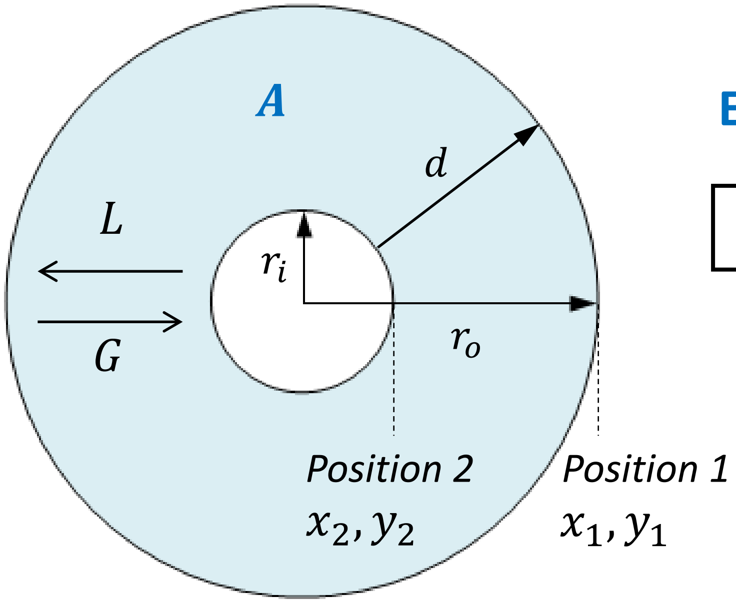
Mean driving force approach

$$\overline{(y - y^*)}_{LM} = \frac{[y_1 - y^*(x_1)] - [y_2 - y^*(x_2)]}{ln\left(\frac{y_1 - y^*(x_1)}{y_2 - y^*(x_2)}\right)}$$

$$\overline{(x^* - \mathrm{x})}_{LM} = \frac{[x^*(y_1) - x_1] - [x^*(y_2) - x_2]}{ln\left(\frac{x^*(y_1) - x_1}{x^*(y_2) - x_2}\right)}$$

RPB separation efficiency

Diffusional approach



Example: gas-film controlled process, dilute case

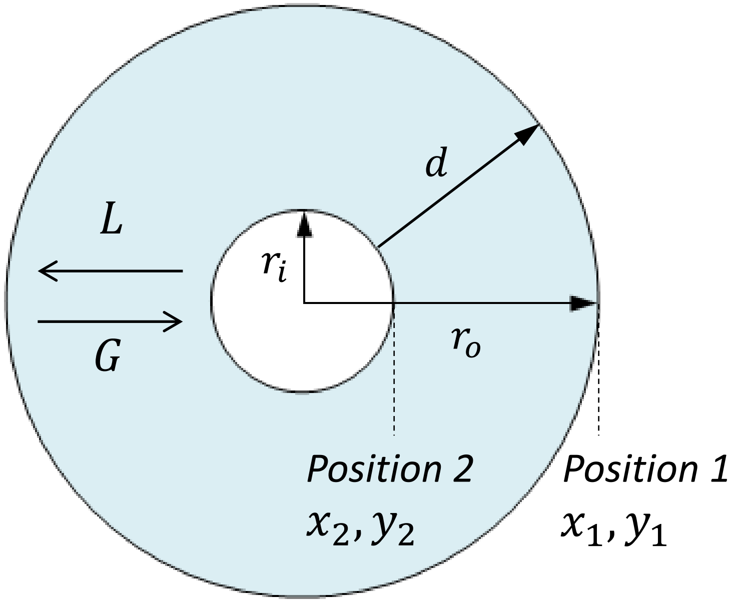
$$\boxed{ATU \times NTU = A_{OG} \times N_{OG} = \boldsymbol{A} = \pi({r_o}^2 - {r_i}^2)}$$

$$N_{OG} = \int_{y_2}^{y_1} \frac{dy}{y - y^*} = \frac{y_1 - y_2}{\overline{(y - y^*)_{LM}}}$$

$$A_{OG} = \frac{A}{N_{OG}} = \frac{G}{(r_o - r_i)\, K_{OG}^0\, a\, p}$$

RPB separation efficiency

Disk hydraulic capacity



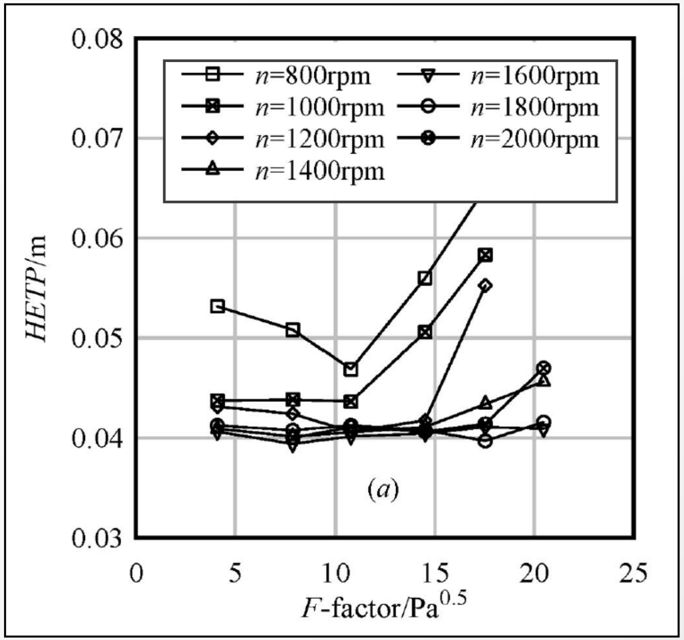
$$F = u_{G,2}\sqrt{\rho_{G,2}}\ [Pa^{0.5}]$$

- Characterized by the F-Factor
- $u_{G,2}$: gas velocity at the eye of the rotor (position 2)
- $\rho_{G,2}$: gas density at the eye of the rotor
- High value of F-Factor indicates high productivity
- Increase in F-factor leads to
  - Increased pressure drop
  - Increased liquid hold-up
  - Variations in ATU and HETP
  - Flooding at some critical upper value of the F-Factor

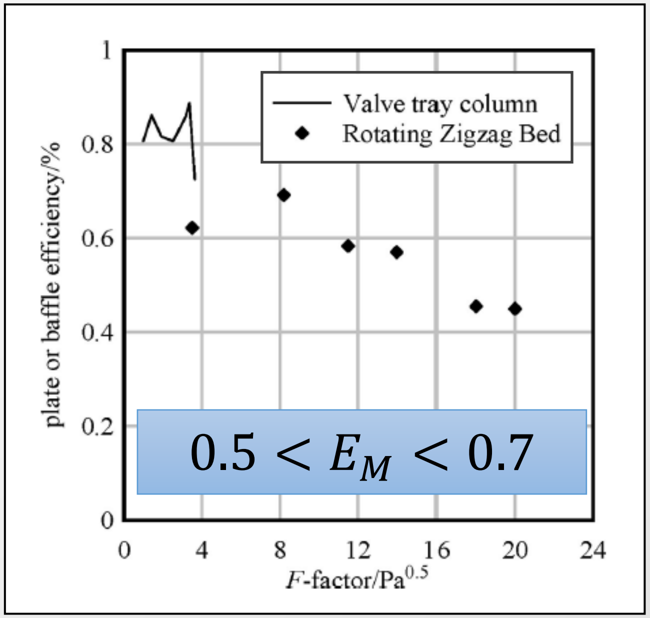
RZB separation efficiency

Equilibrium-stage approach:

$$d = HETP \cdot NTP$$

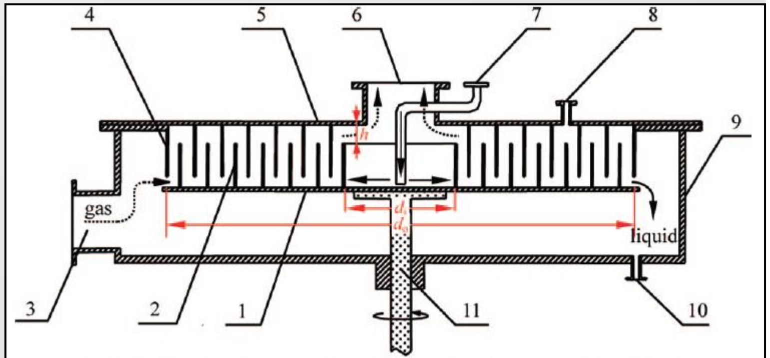


$$0.04 < HETP < 0.07m$$



$$0.5 < E_M < 0.7$$

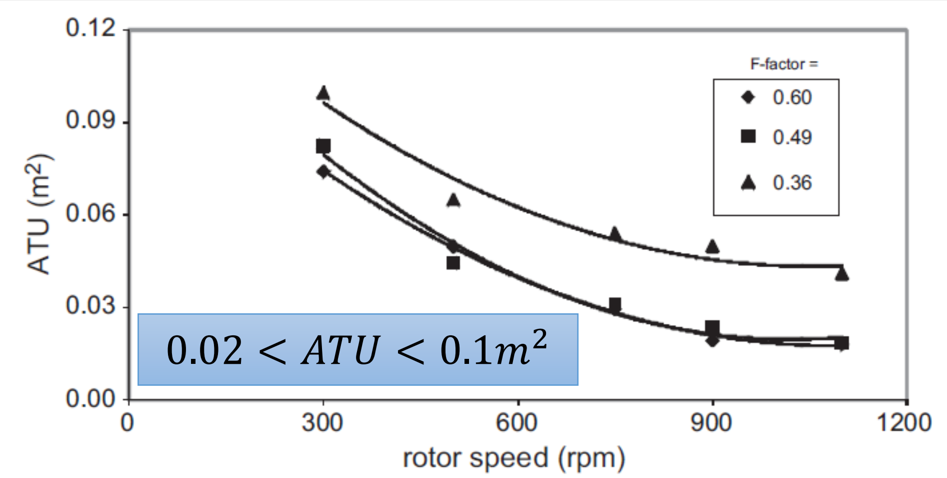
"Rotating zigzag bed"→



1-rotational disc 2-rotational baffle 3-gas inlet 4-stationary baffle 5-stationary disc 6-gas outlet 7-liquid inlet 8-Intermediate feed 9-liquid outlet 10-rotor casing 11-rotating shaft

Wang et al., Ind. Eng. Chem. Res. 2008, 47, 8840–8846

RZB separation efficiency

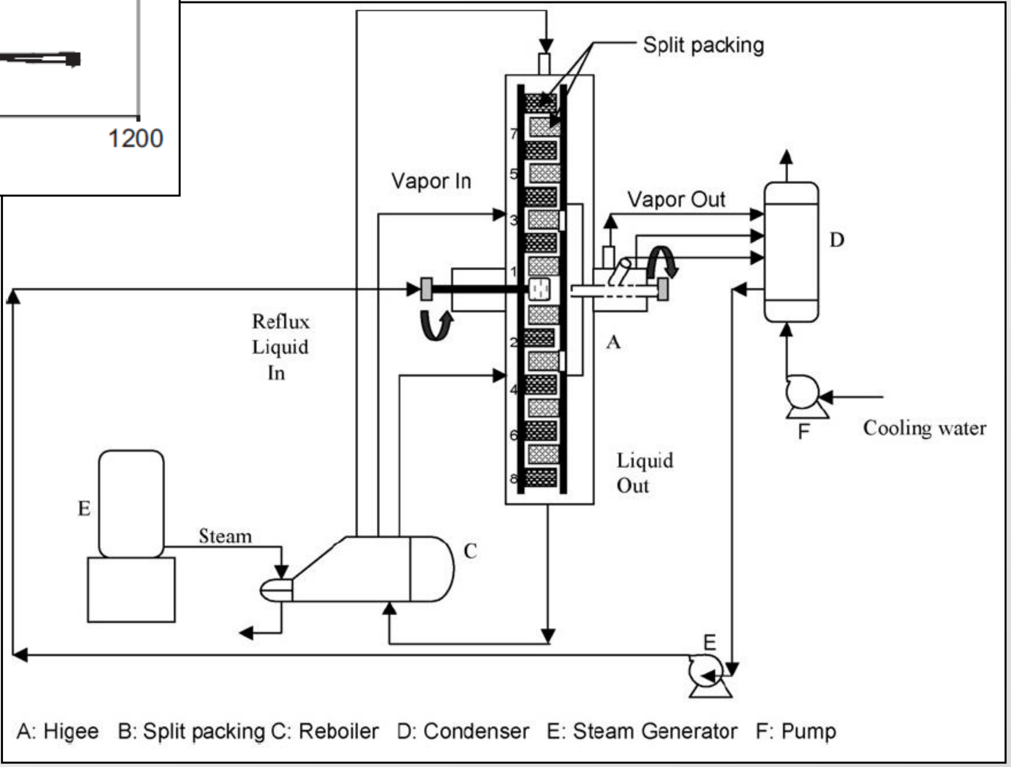


$0.02 < ATU < 0.1m^2$

Diffusional approach:

$$A = ATU \cdot NTU$$

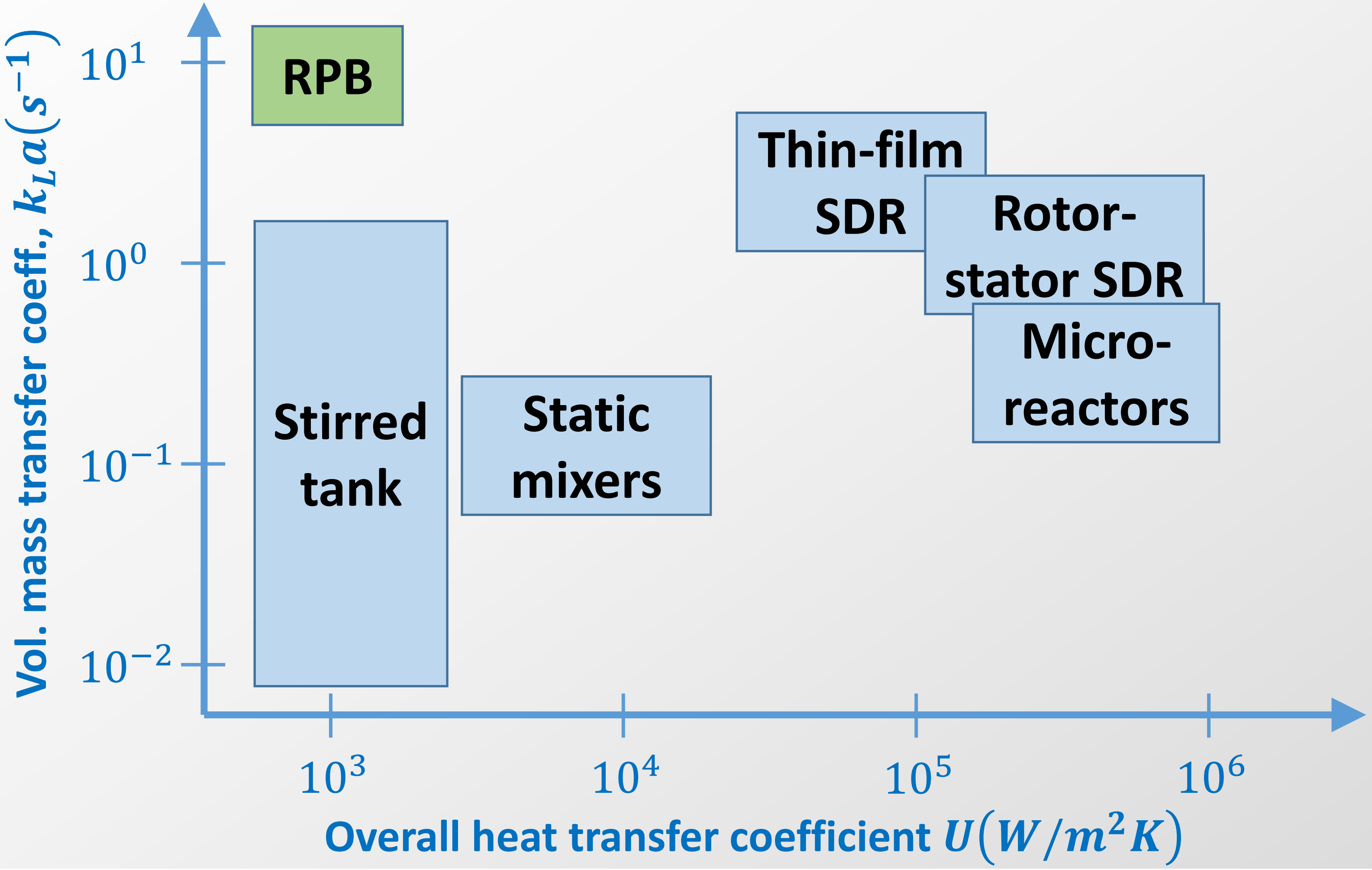
MeOH / Water, total reflux



Mondal et al., Chem. Eng. Res. Dev 90 (2012), 453–457

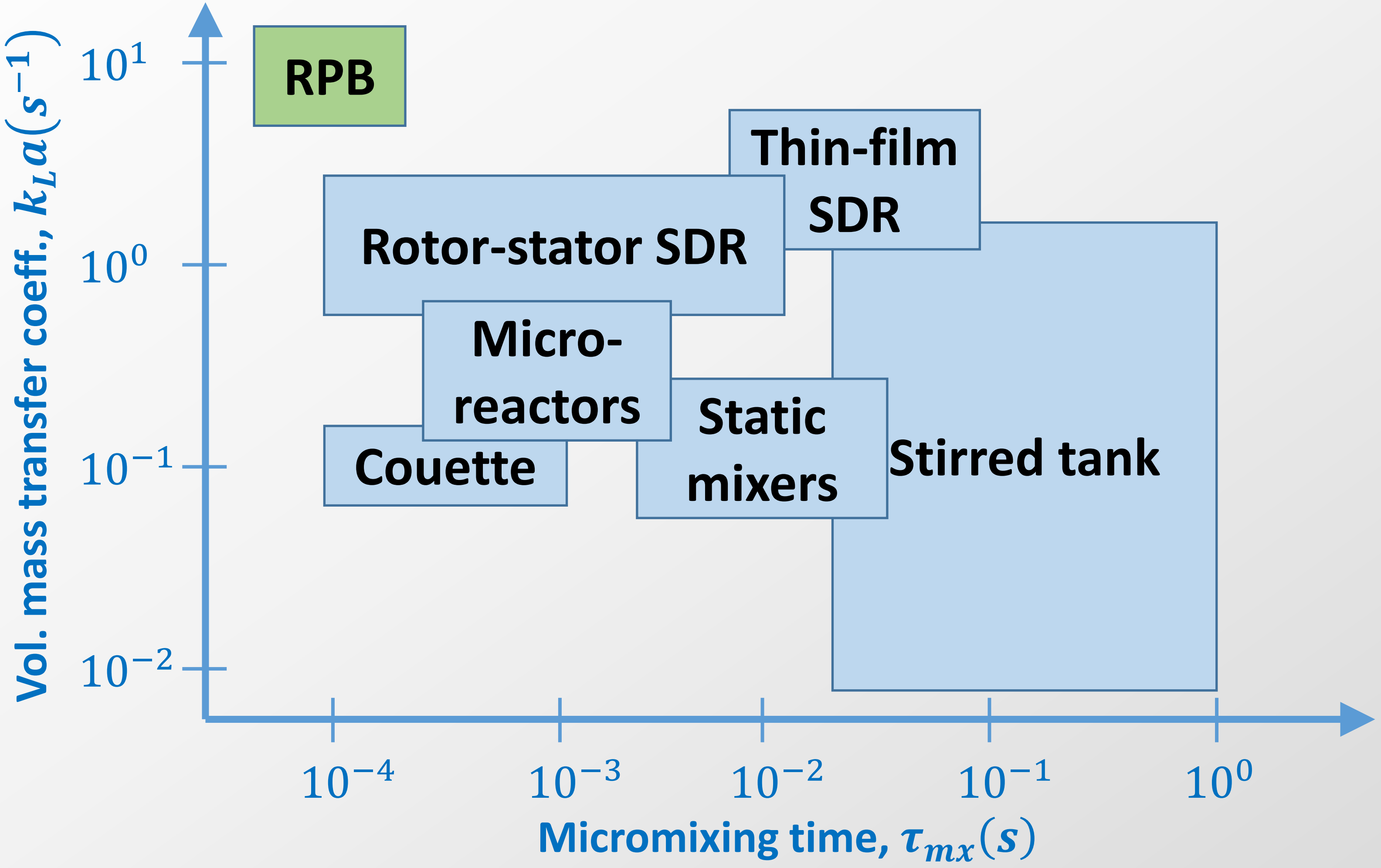
Reactor mapping

Approximate mass and heat transfer space



Reactor mapping

Approx. mass transfer and mixing time space

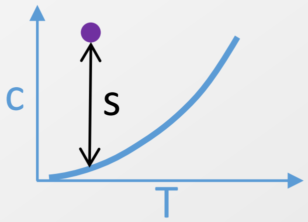


2.1 Higee contactors

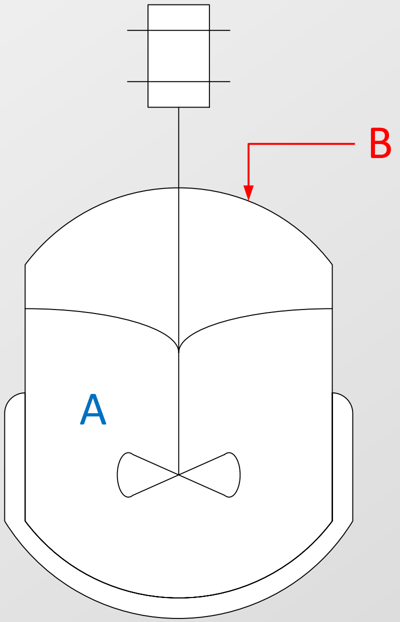
2.1.6 Industrial applications of Higee contactors

Precipitation in batch reactor

$$\boxed{A + B \rightarrow P}$$

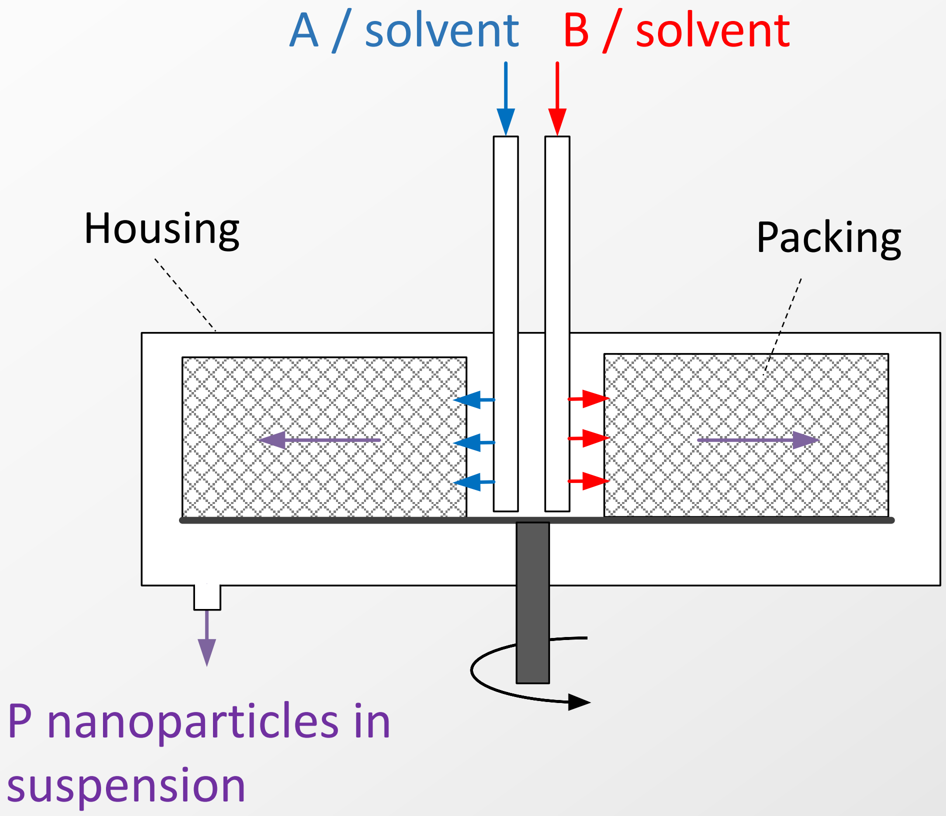


- Very fast reactions (often acid-base type)
- Extremely high supersaturation due to very low product (P) solubility
- Batch reactor:
  - $\tau_{mx} \gg \tau_{rx} \rightarrow$ Broad particle size distribution due to uneven concentration (as a result of slow mixing) and strong gradient of shear rate
  - Difficult scale-up due to non-uniform environment



Precipitation in RPB

$$\boxed{A + B \rightarrow P}$$



- $\tau_{rx} \cong 1ms, \tau_{mx} \cong 0.1ms$
- $\tau_{mx} < \tau_{rx}$
- Narrow PSD thanks to uniform concentrations (as a result of fast mixing)
- Small particle size resulting from high nucleation rate (high supersaturation)
- Scale up easier than for batch

RPB industrial applications

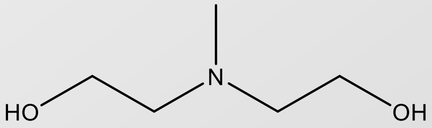
- SO_2 removal (desulfurization) using ammonia-based wet scrubbing process.
  - Poor mass transfer efficiency → large packed columns or spray towers
  - RPB used to increase mass transfer and reduce the size of the columns
  - Decrease in capital investment, volume and energy consumption

$$SO_2 + H_2O + x\ NH_3 \rightarrow (NH_4)_xH_{2-x}SO_3$$

$$(NH_4)_xH_{2-x}SO_3 + \frac{1}{2}\ O_2 + (2-x)\ NH_3 \rightarrow (NH_4)_2SO_4$$

Ammonium sulfate (fertilizer)

- Selective absorption of H_2S over CO_2 using methyldiethanolamine as a solvent
  - CO_2 co-absorption reduced from 79.9% to 8.9%
  - Equipment volume reduced from 36.1 m^3 to 3.4m^3
  - Packing volume reduced from 14 m^3 to 0.3 m^3.



RPB industrial applications

- Seawater de-aeration
  - To avoid corrosion and bacterial growth
  - 32m high vacuum tower → 1.4m rotating strippers
  - Ideal for off-shore operation

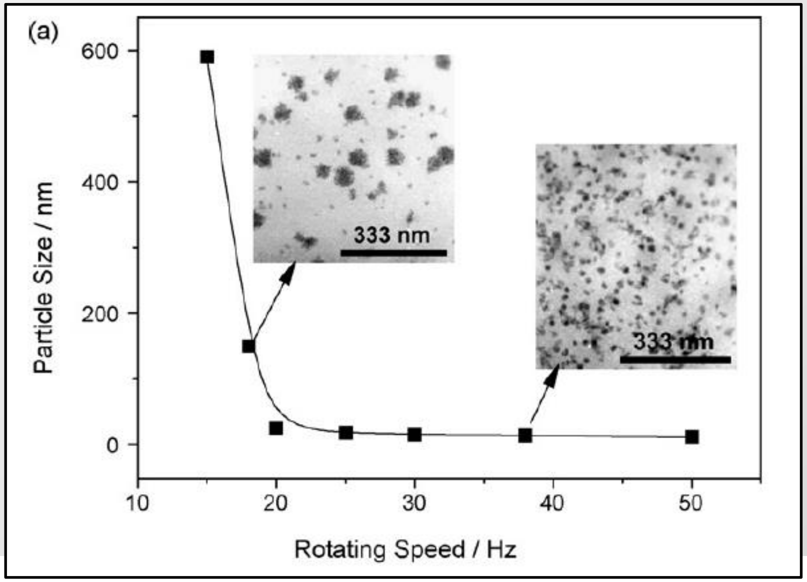
- Monodisperse $CaCO_3$ nanoparticles*
  - $CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$
  - Need narrow PSD and small mean particle size (<20 nm) for increased stability and transparency of detergents (main application)
  - Benefits: increased monodispersity and stability, smaller average particle size (6 nm), narrower size distribution, higher TBN**, shortened carbonation time.
  - Production volume in China ~36 ktons/y

**Kang et al., Powder Technology 325 (2018) 405–411*
***Total Base Number*

RPB potential applications

- Nanoparticles for pharmaceuticals using reactive precipitation or high-gravity anti-solvent precipitation (HGAP)
  - ✓Better control of particle size
  - ✓Improved bioactivities (faster dissolution rate)
  - ✓Less need for complex solubilizers
  - ✓Higher fraction of fine particles

Production of benzoic acid (model compound for the investigation of reactive precipitation of pharmaceuticals in RPB) using sodium benzoate and HCl
→ nanoparticles of ~10 nm



Zhao et al., Chemical Engineering Journal 156 (2010) 588–593

HOCl production in RPB

- Process steps
  1. Cl_2 absorption into aq. solution of NaOH (liquid-side mass transfer limited)
  2. Reaction of Cl_2 with NaOH:

$$\boxed{Cl_2(g) + NaOH(l) \rightarrow NaCl(l) + HOCl(l)}$$

  3. HOCl desorption (gas-side mass transfer limited)
  4. HOCl liquid-phase side reaction (decomposition):

$$\boxed{3\ HOCl + 3\ NaOH \rightarrow NaClO_3 + 2NaCl + 3H_2O}$$

⇨Need to desorb HOCl before it decomposes in the liquid phase

- Traditionally produced in large spray-towers (high capital and operating costs)

HOCl production in RPB

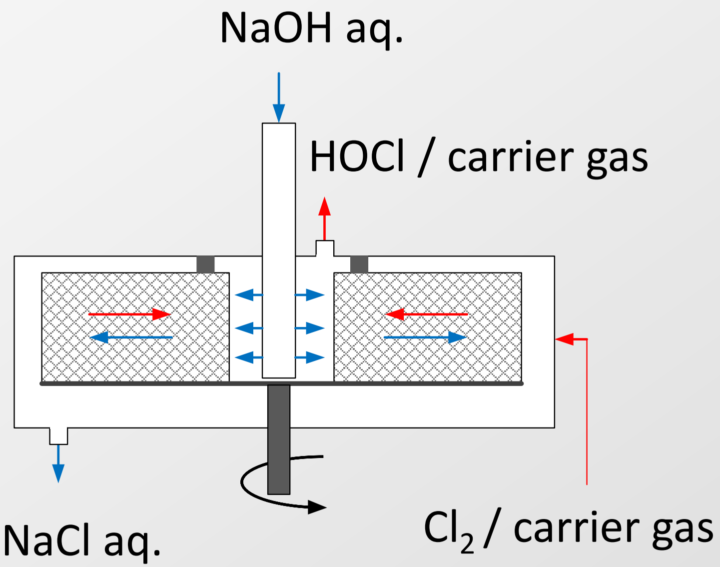
PI solution/benefits

Mass transfer intensification:

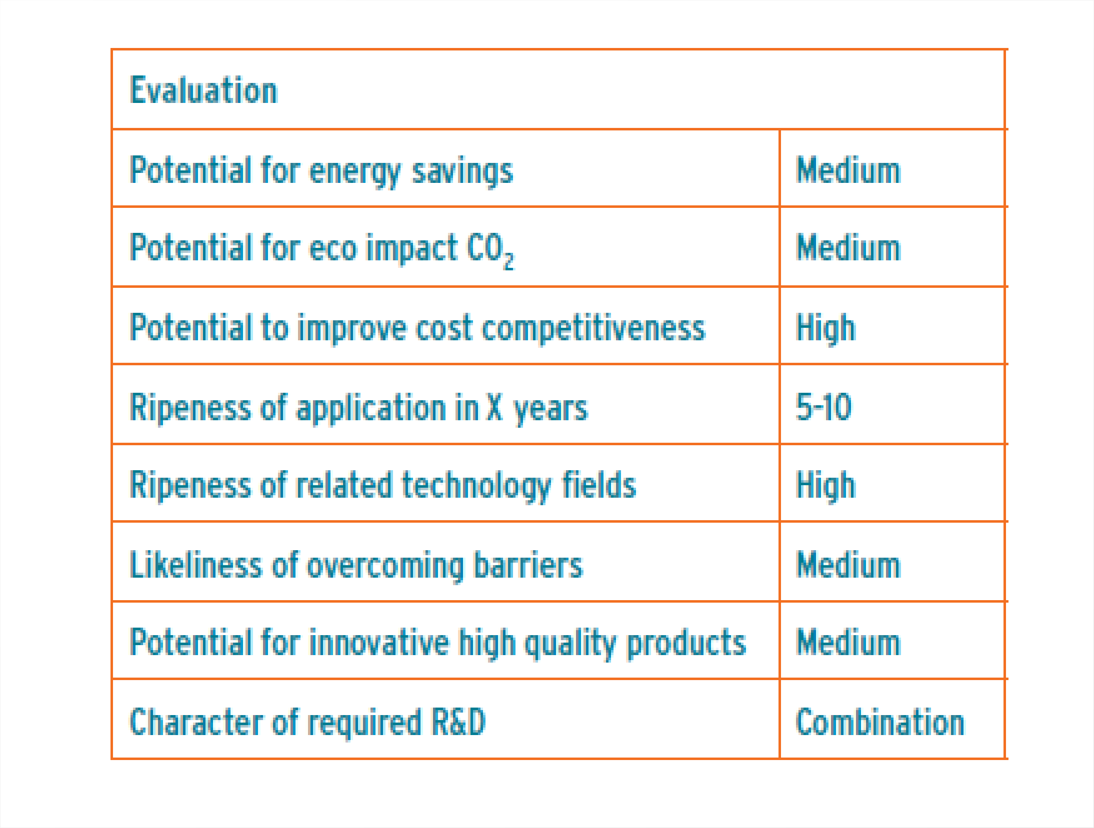
- ✓ Quick absorption of Cl_2
- ✓ Quick desorption of HOCl before it has time to decompose

Result

- ✓ >10% yield increase
- ✓ 40-fold decrease in equipment size
- ✓ 2-fold decrease in stripping gas requirements
- ✓ equipment investment cut by 70%
- ✓ Cl_2 recycle volume reduced by 50%



RPB technology assessment*

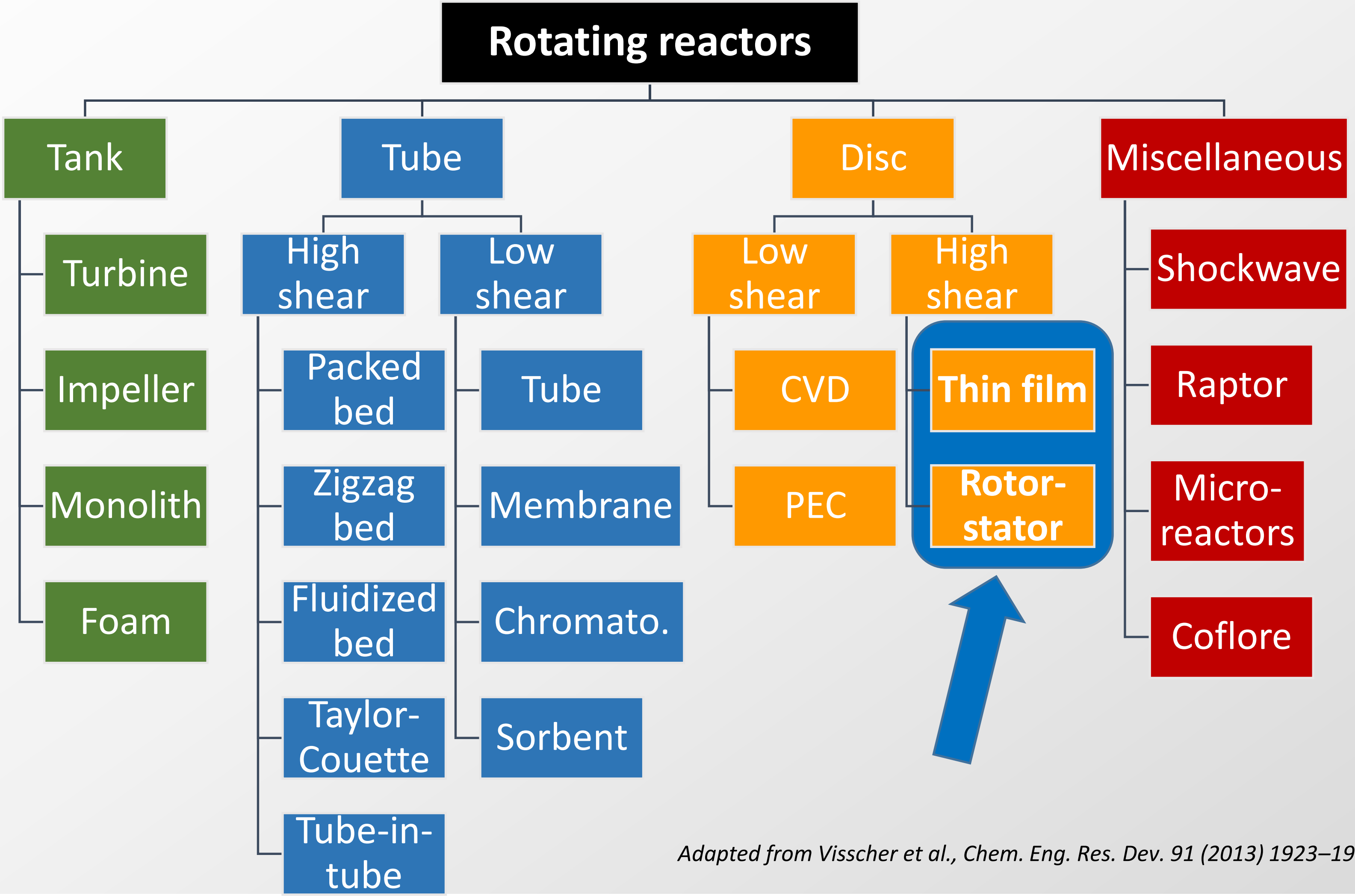


Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO_2	Medium
Potential to improve cost competitiveness	High
Ripeness of application in X years	5-10
Ripeness of related technology fields	High
Likeliness of overcoming barriers	Medium
Potential for innovative high quality products	Medium
Character of required R&D	Combination

**European roadmap for process intensification, 2009*

2.2 Spinning disk reactors (SDR)

Rotating reactors classification



Rotating reactors

Tank

- Turbine
- Impeller
- Monolith
- Foam

Tube

- High shear
  - Packed bed
  - Zigzag bed
  - Fluidized bed
  - Taylor-Couette
  - Tube-in-tube
- Low shear
  - Tube
  - Membrane
  - Chromato.
  - Sorbent

Disc

- Low shear
  - CVD
  - PEC
- High shear
  - **Thin film**
  - **Rotor-stator**

Miscellaneous

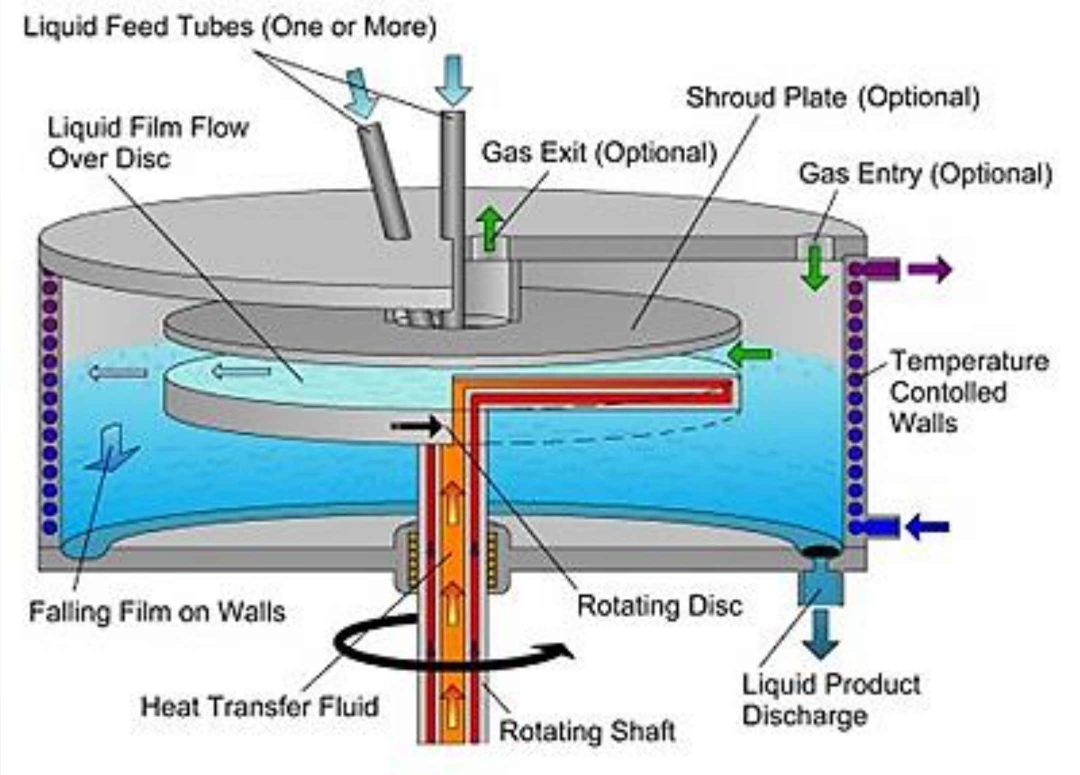
- Shockwave
- Raptor
- Micro-reactors
- Coflore

Adapted from Visscher et al., Chem. Eng. Res. Dev. 91 (2013) 1923–1940

2.2 Spinning disk reactors

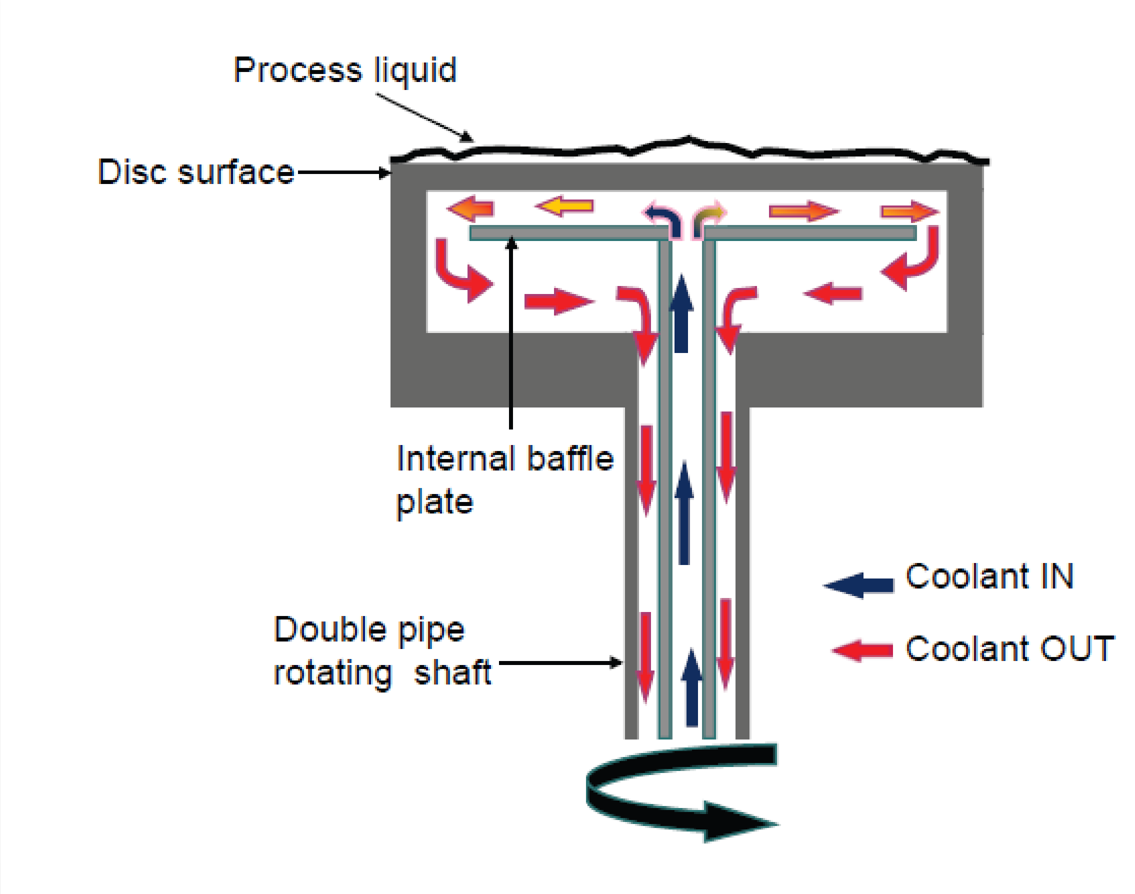
2.2.1 Thin-film spinning disk reactor (TF-SDR)

Scheme of thin-film SDR



Boodhoo, K. Spinning Disc Reactor for Green Processing and Synthesis. In Process Intensification for Green Chemistry; John Wiley & Sons, Ltd.: Chichester, UK, 2013; pp. 59–90.

Spinning disk reactor
Internal heat transfer system



Boodhoo and Harvey (2013)

TF-SDR working principles

- High-acceleration environment created by rotating horizontal disk surface
- Liquid(s) introduced a few millimeters above center of disc surface
- Disk may be equipped with internal heat transfer system
- High centrifugal field (up to 1000 g at disk edge) propels the liquid to disc edge as a very thin, highly sheared film
- After leaving disk edge, liquid is quenched at the walls (temperature controlled)
- Possibility to control reactor atmosphere (e.g. inert gas)

TF-SDR characteristics

- Fast mixing ($10^{-2}s < \tau_{mx} < 10^{-1}s$)
- High heat transfer capability ($5 - 50\ kW/m^2K$)
- Fast mass transfer
  - k_L order of $10^{-4} - \ 10^{-3}\ m/s$
  - a_{GL} order of $10^3\ \ m^2/m^3$
- Low axial dispersion (~plug flow)
- Short residence time (~$0.1 – \ 2\ s$)
- High surface-to-volume ratio ($5 \cdot 10^3 - 15 \cdot 10^3\ m^2/m^3$)
- Very thin films ($50 - 500\ \mu m$)
- High shear rates
- Easy scale up (compared to batch reactor)

Mass and heat transfer correlations

Gas-liquid mass transfer

$$\frac{k \cdot R}{D} = 1.6 \cdot 10^{-3} \left(\frac{\omega R^2 \rho}{\mu}\right)^{0.94} \left(\frac{Q\rho}{\mu R}\right)^{0.24} \left(\frac{\mu}{\rho D}\right)^{0.5}$$

Heat transfer*

$$h = \frac{5}{3}\lambda \left(\frac{2\pi\rho R^2 \omega^2}{3Q\mu}\right)^{1/3}$$

**Nusselt treatment, Aoune and Ramshaw, Int. J. Heat Mass Tran., 42, 2543–2556 (1999)*

Spinning disk reactor

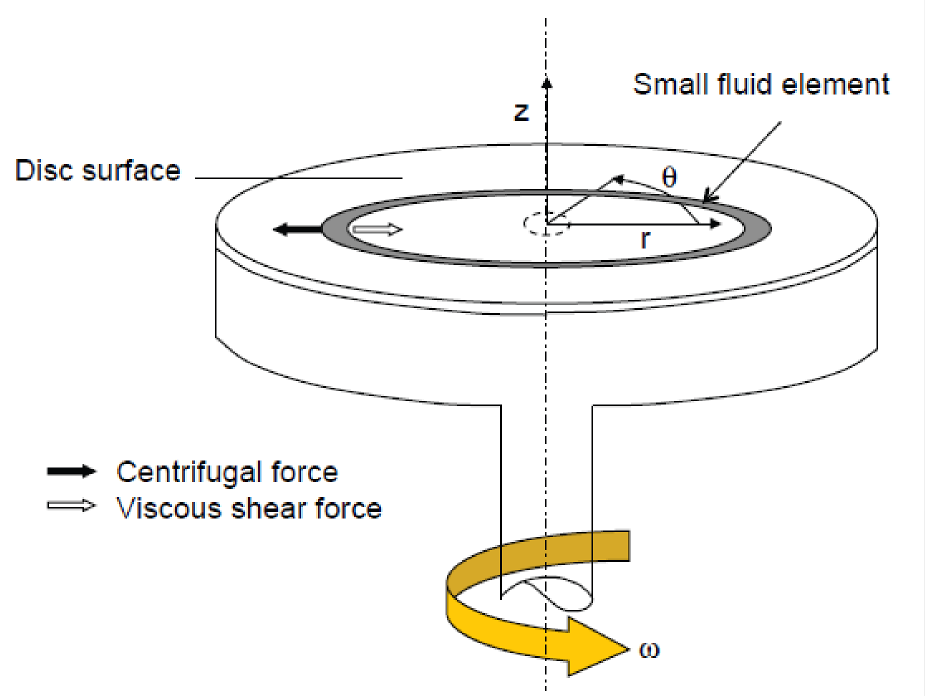
Typical operating parameters

- Disk diameter 0.1 - 1 m
- Rotational speed 200 - 6000 rpm
  - 0.15 m: 6000 rpm max
  - 1 m: 1000 rpm max
- Disk surface
  - Smooth, grooves, meshed, non-stick surface, etc
- Disk material
  - SS, brass, glass
- Liquid flowrates: 2 - 700 l/h
- Temperature: -20 to 300°C
- Pressure: up to 10 bar

Hydrodynamics in TF-DSR

Smooth fully developed laminar flow of Newtonian liquids

Force balance at steady state: $-\omega^2 \mathrm{r} = \nu \dfrac{\partial^2 v_r}{\partial z^2}$



$\omega\ [rad/s] = 2\pi\ [rad/rotation] \cdot N\ [rotations/s]$

Film thickness

$$\delta(r) = \left(\frac{3}{2\pi}\frac{\nu Q}{\omega^2 r^2}\right)^{1/3}$$

Mean residence time

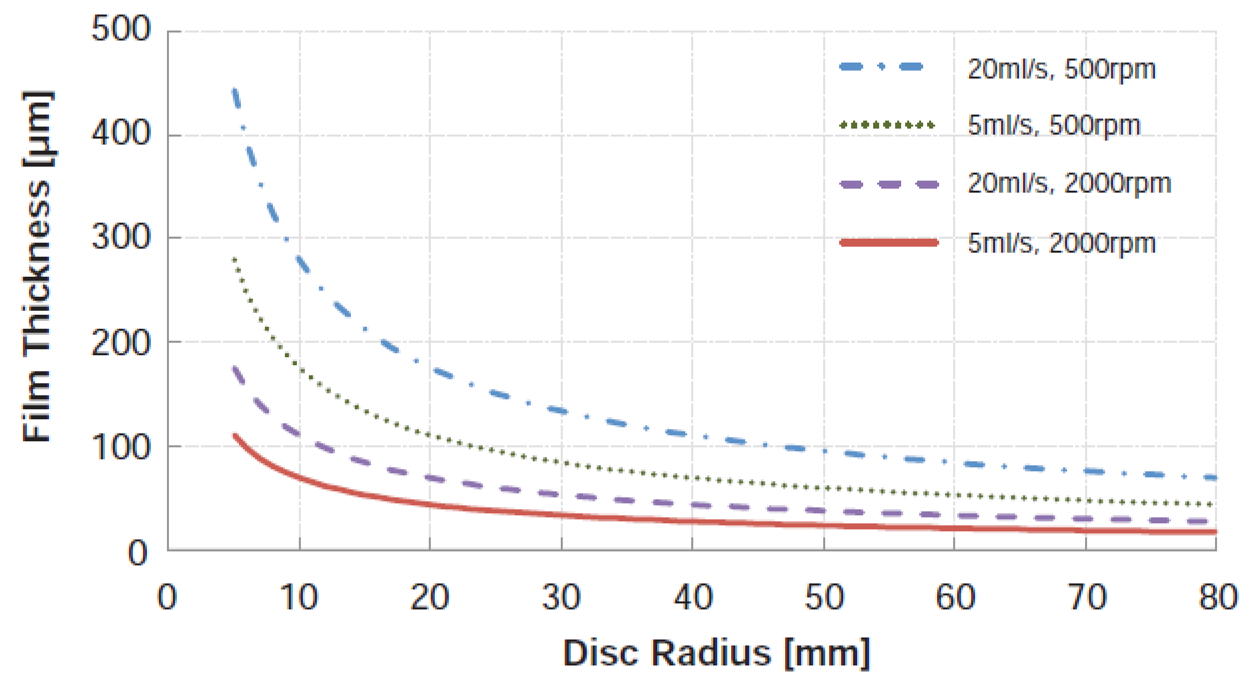
$$\tau = \left(\frac{81\pi^2}{16}\frac{\nu}{\omega^2 Q^2}\right)^{1/3} \left({r_0}^{4/3} - {r_i}^{4/3}\right)$$

Shear rate

$$\dot{\gamma}(r,z) = \frac{dv_r(r,z)}{dz} = \left(\frac{3}{2\pi}\frac{Q\omega^4 r}{\nu^2}\right)^{1/3} \left(1 - \frac{z}{\delta}\right)$$

Film thickness vs Q and ω

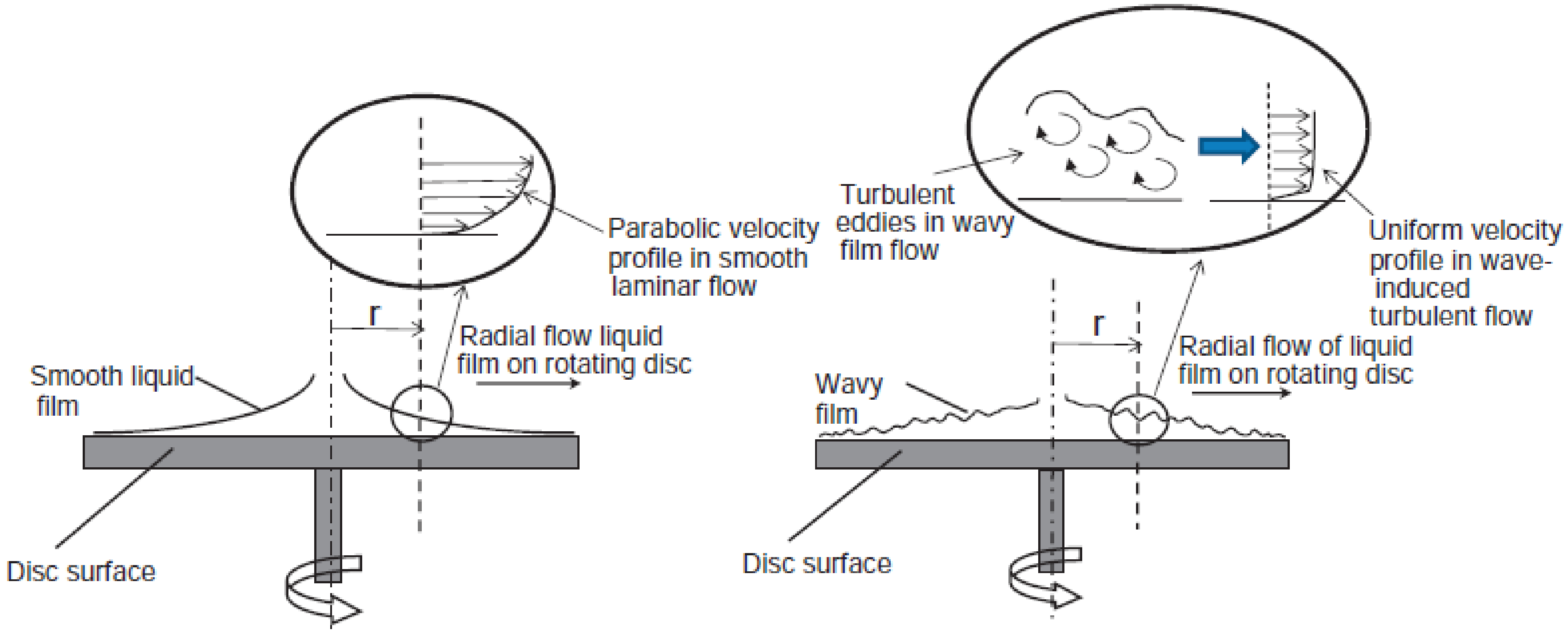
$$\delta \propto Q^{1/3}\omega^{-2/3}$$



Wavy films

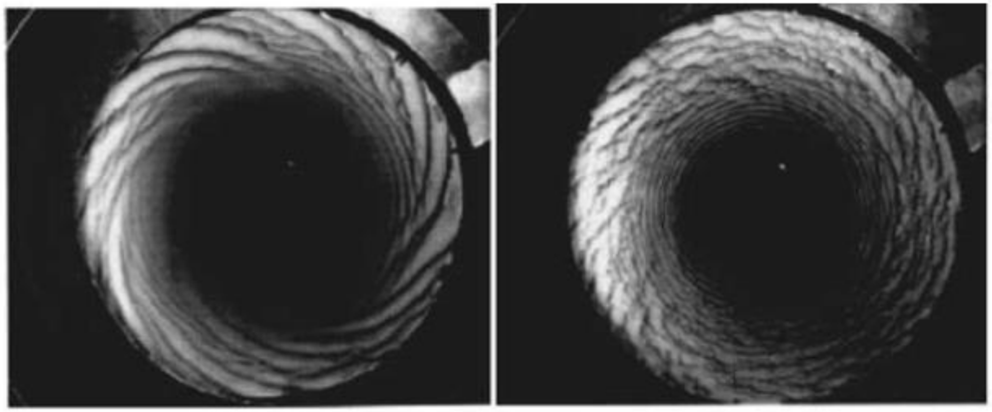
- Increase in mass and heat transfer due to small film dimensions (accelerated diffusion and conduction)
- In addition, waves occur which increase surface area and turbulence (rippling effect), resulting in even higher mass and heat transfer rates
- Textured surfaces (grooves, surface roughness) promote wave formation

Smooth vs wavy film in SDRs



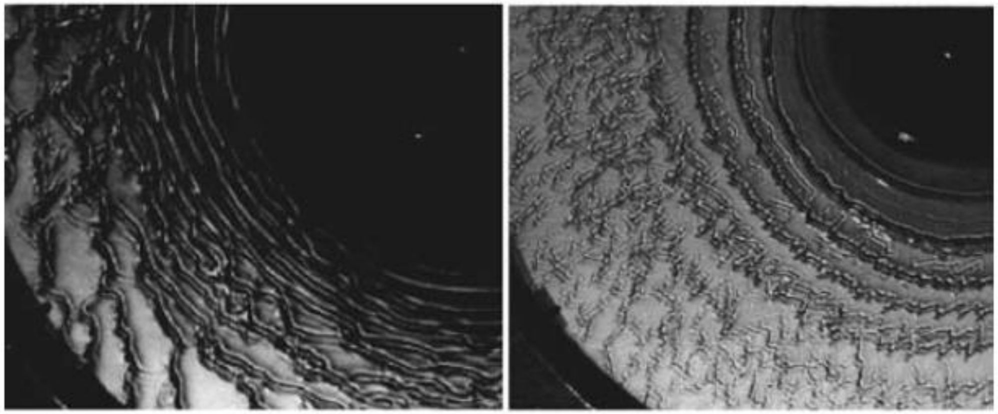
Smooth laminar film **Wavy film with induced turbulence**

Wave formation and propagation



(a) ω=10 rad. s^{-1}, Q=19 cm^3/s

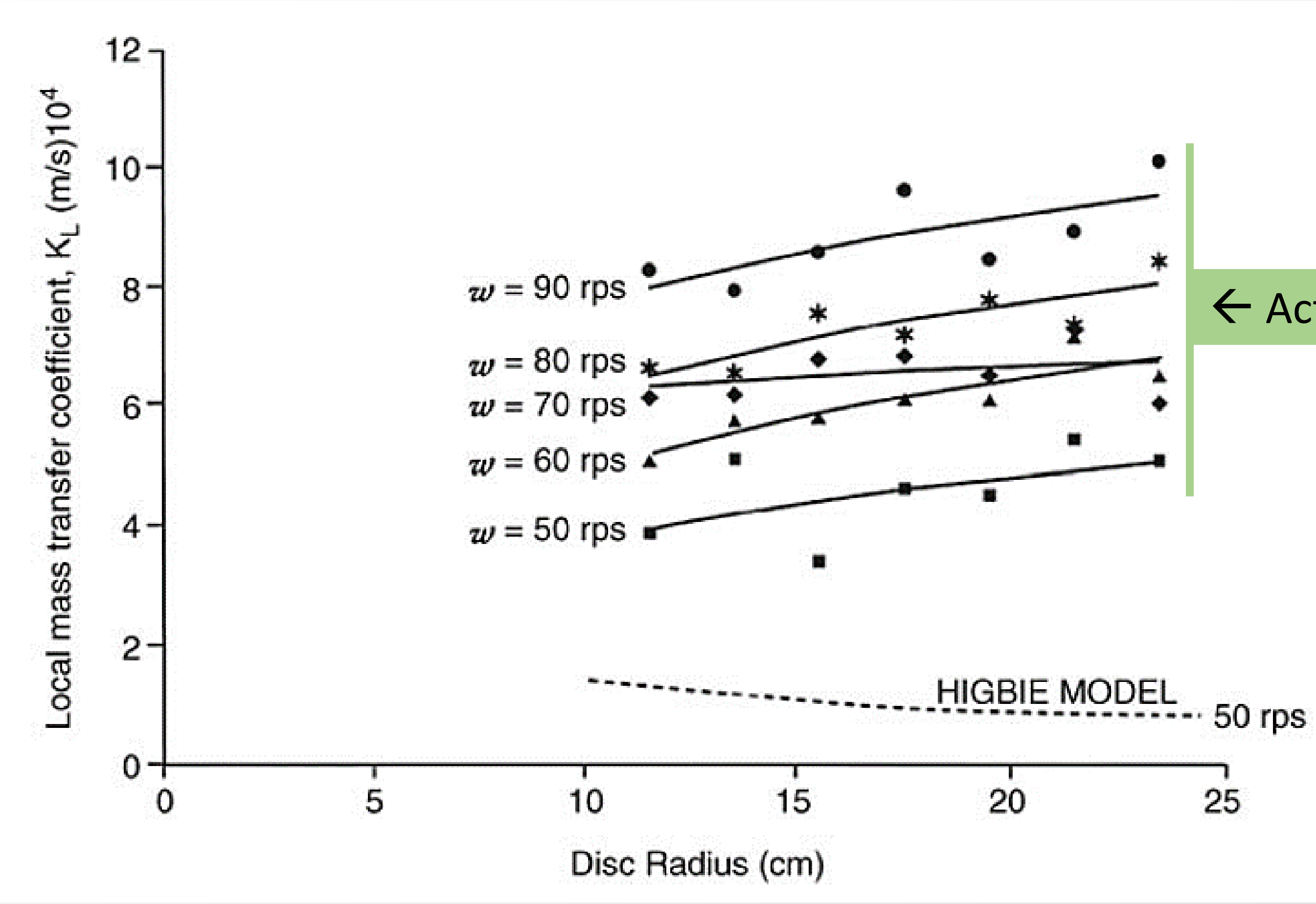
(b) ω=20 rad. s^{-1}, Q=19 cm^3/s



(c) ω=20 rad. s^{-1}, Q=19 cm^3/s

(d) ω=60 rad. s^{-1}, Q=19 cm^3/s

Mass transfer enhancement by wavy flow



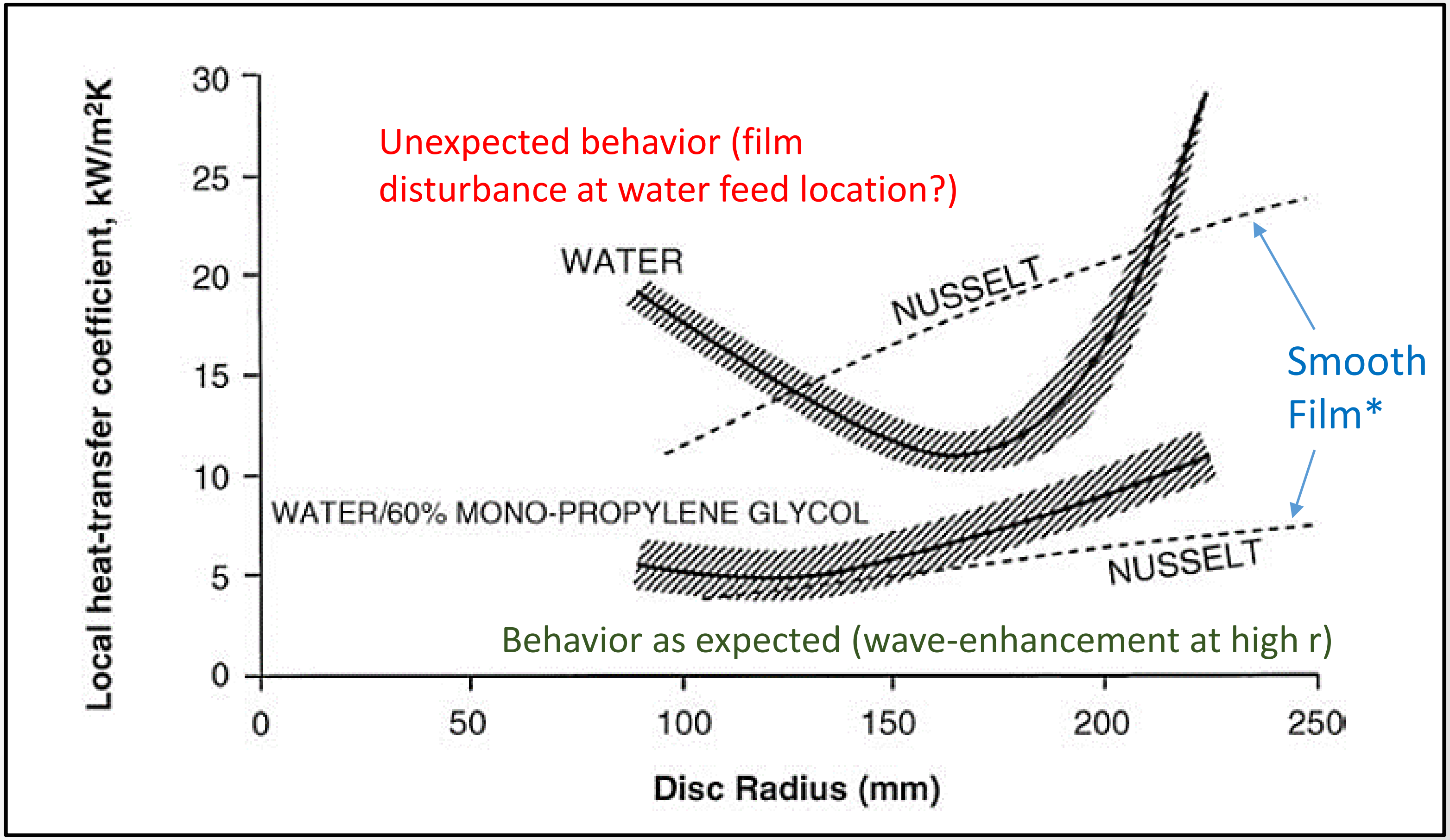
← Actual film

← Smooth film, penetration theory

$$k_L = \sqrt{\frac{D}{\pi\ \tau_c}}$$

Optional

Heat transfer in TF-SDR



Unexpected behavior (film disturbance at water feed location?)

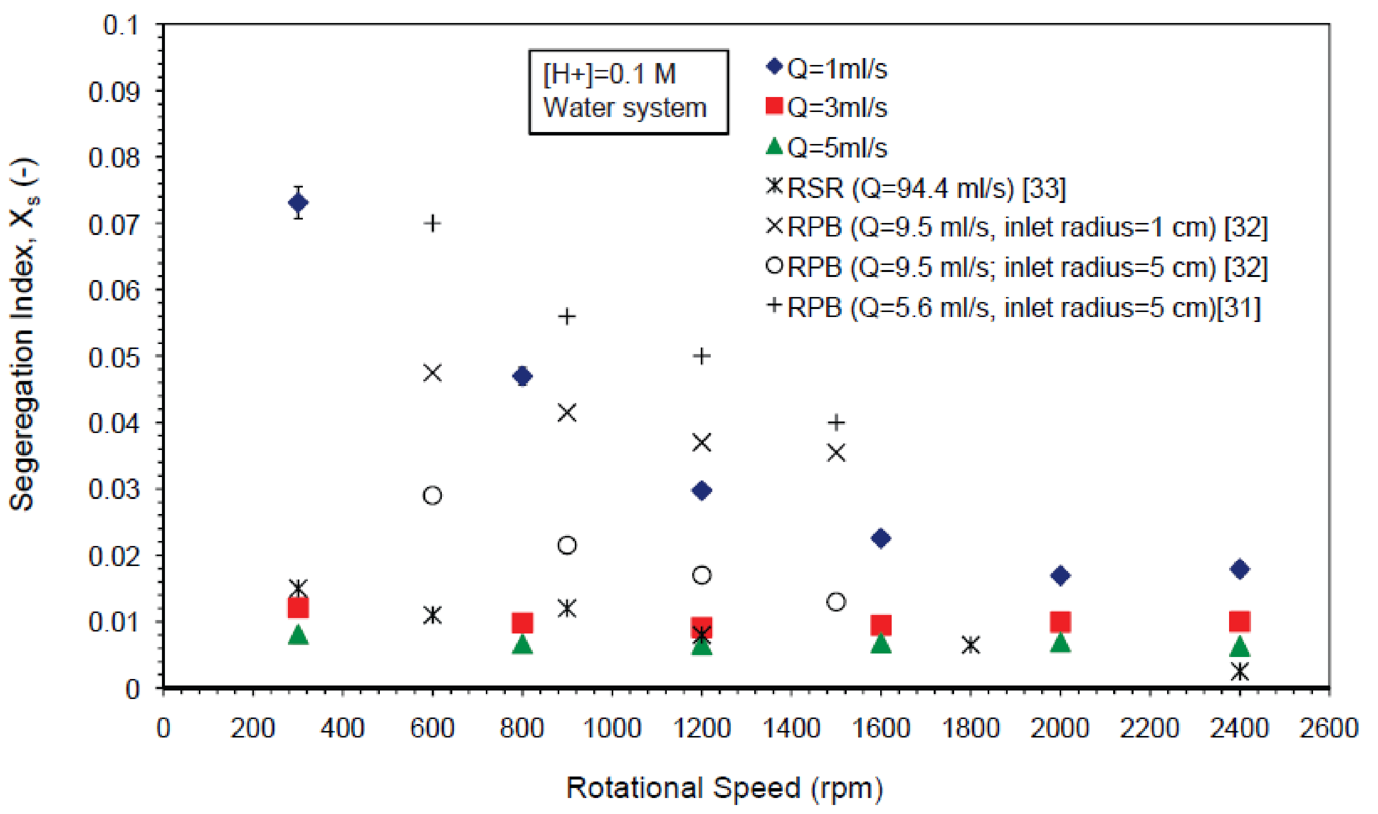
Smooth Film*

Behavior as expected (wave-enhancement at high r)

Aoune and Ramshaw, Int. J. Heat Mass Tran., 42, 2543–2556 (1999)

$$* \; h = \frac{5}{3}\lambda\left(\frac{2\pi\rho R^2\omega^2}{3Q\mu}\right)^{1/3}$$

Segregation index in SDR vs other reactors



SDR at 1 ml/s: potential film breakdown at this low flowrate

RSR: rotor-stator spinning disk reactor

Boodhoo and Al-Hengari,. Chem. Eng. Technol., 35(7), 1229–1237 (2012).

Some TF-SDR applications

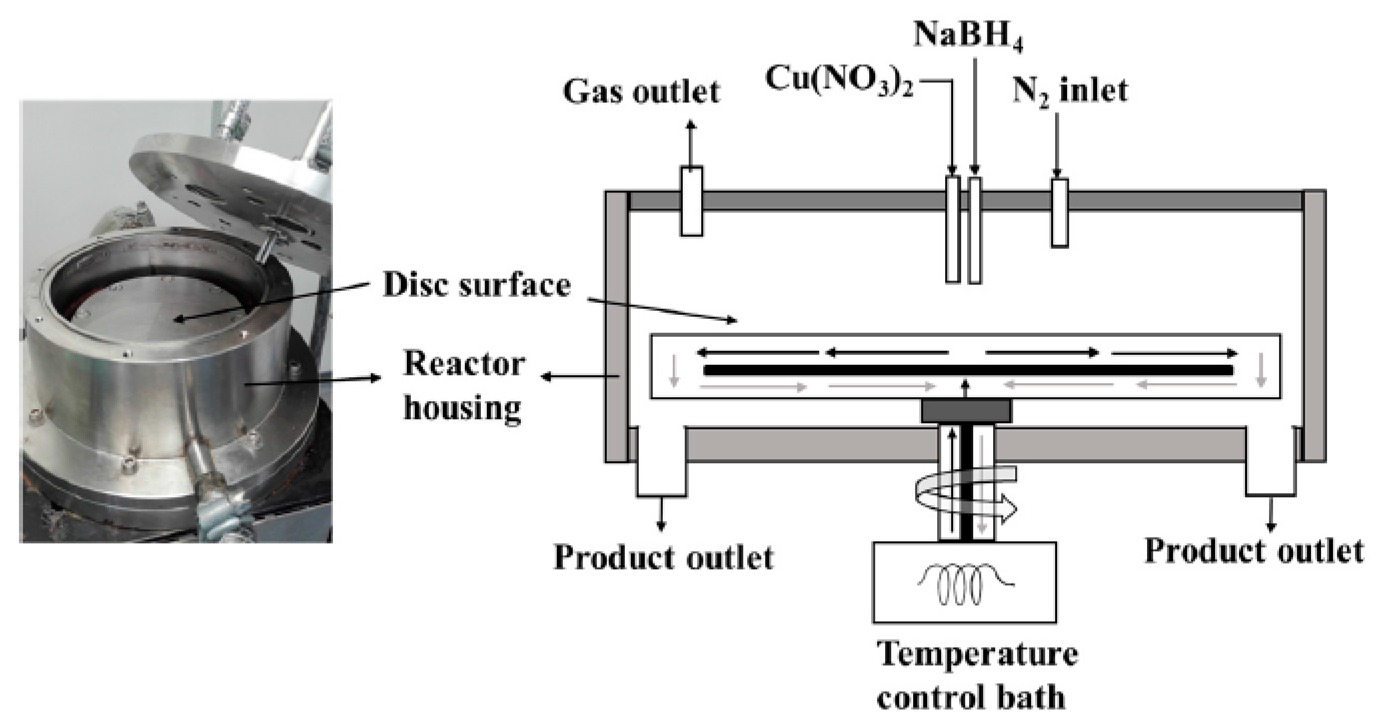
- Polymerization
  - ✓ Mass and heat transfer
  - ✓ Shear rate for good mixing at high viscosity (shear thinning polymers)
- Polycondensation
  - ✓ High mass transfer for fast volatile removal
- Photopolymerization
  - ✓ Low film thickness → efficient UV penetration
- Rapid polymer devolatilization
  - ✓ High liquid/gas mass transfer

- Precipitation (nanoparticles)
  - ✓ Low mixing time → high and uniform supersaturation
- Heterogeneous catalytic reactions (catalytic disk)
- Fast and exothermic reactions
  - ○ High mass/heat transfer, plug flow

TF-SDR application example

Cu nanoparticles for low T MeOH synthesis

$$Cu(NO_3)_2 + 2NaBH_4 + 6H_2O \rightarrow Cu\downarrow + 7H_2 + 2NaNO_3 + 2B(OH)_3$$

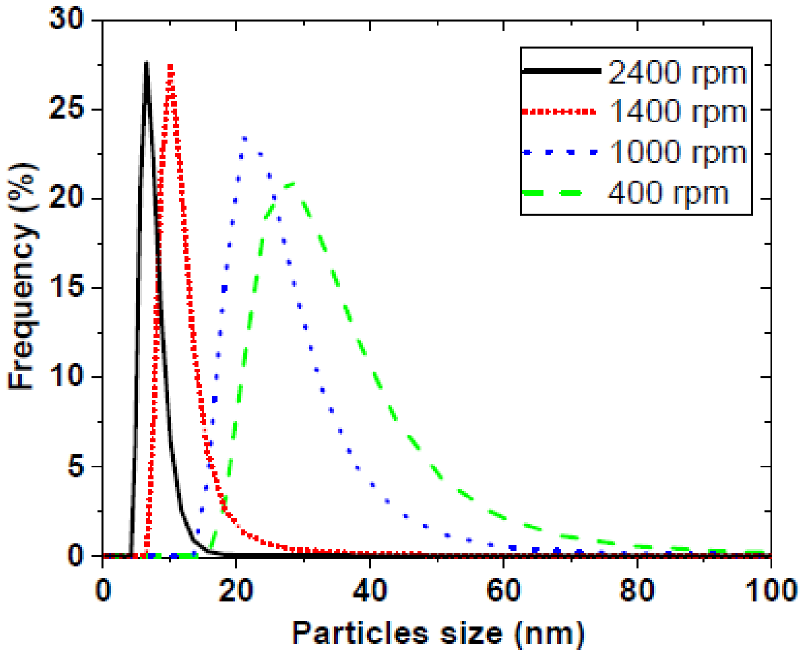


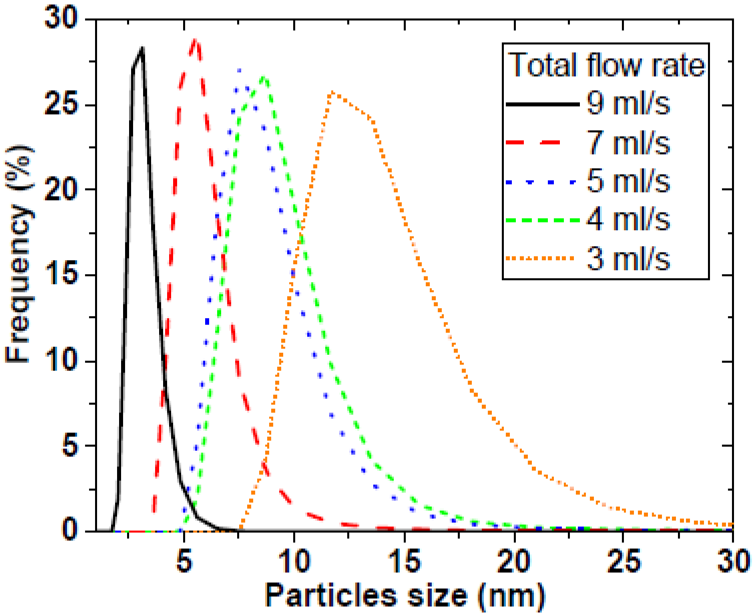
Ahoba-Sam et al., Materials 2018, 11, 154

TF-SDR application example

Cu nanoparticles for low T MeOH synthesis

$$Cu(NO_3)_2 + 2NaBH_4 + 6H_2O \rightarrow Cu\downarrow + 7H_2 + 2NaNO_3 + 2B(OH)_3$$





High ω and Q ⇨ high Bo, low $\bar{\tau}$, low τ_{mx}

High Bo ⇨ narrow PSD

Low $\bar{\tau}$ ⇨ reduce growth and agglomeration

Low τ_{mx} ⇨ uniform supersaturation ⇨ narrow PSD

Low τ_{mx} ⇨ high supersaturation ⇨ nucleation > growth ⇨ low d_p

Scale up

Smooth fully developed laminar flow of Newtonian liquids

- **Constant conversion:** $X_{plant} = X_{lab}$
    - $\tau_{plant} = \tau_{lab}$
    - $\delta_{plant} = \delta_{lab}$

  $\rightarrow \omega_{plant} = \omega_{lab}$ and $r_{plant} = r_{lab}\sqrt{\frac{Q_{plant}}{Q_{lab}}}$

- **Non-constant conversion:** $X_{plant} = f \cdot X_{lab}$
    - Assumptions
        - $\tau_{plant} = f \cdot \tau_{lab}$ (for zero-order process)
        - $\delta_{plant} = \delta_{lab}$

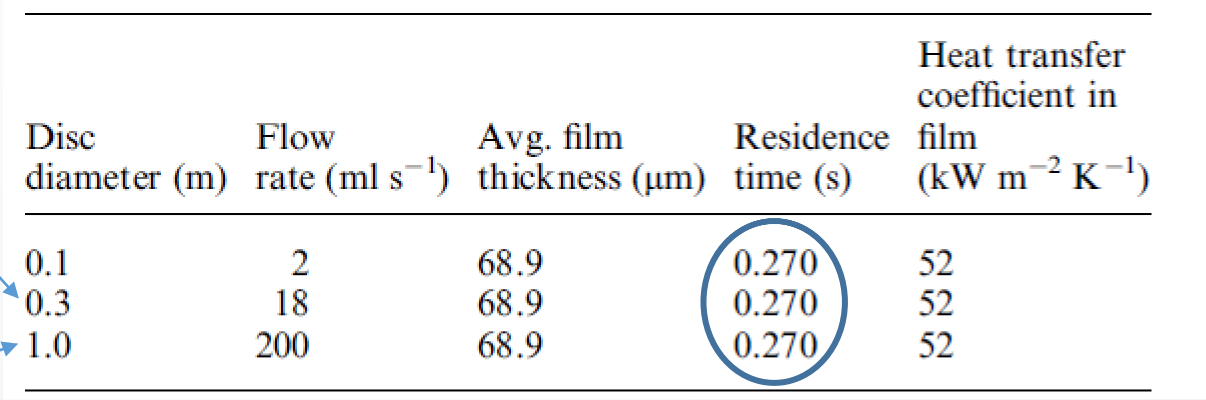
  $\rightarrow \omega_{plant} = \omega_{lab}\frac{1}{\sqrt{f}}$ and $r_{plant} = r_{lab}\sqrt{f \cdot \frac{Q_{plant}}{Q_{lab}}}$

Scale up examples

Constant conversion[1]

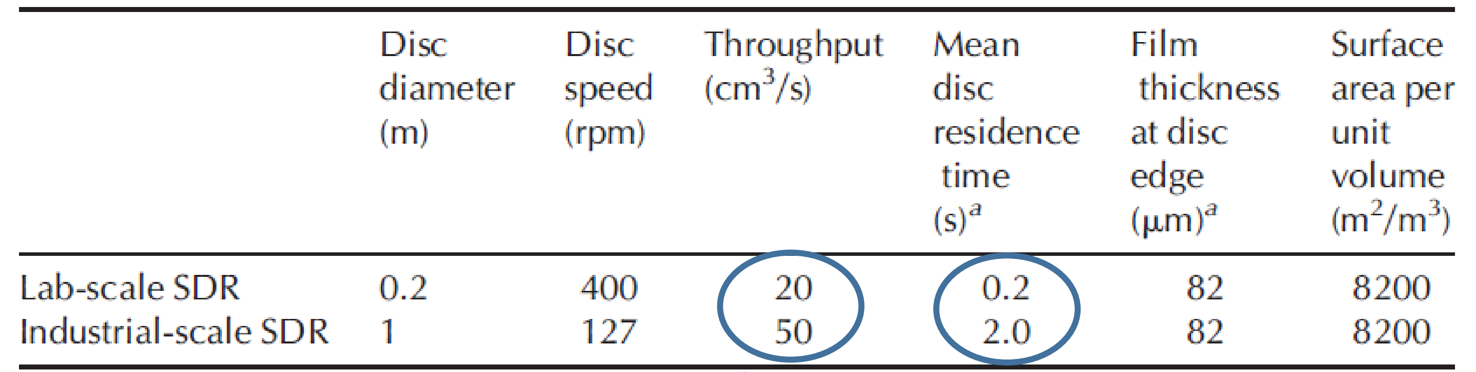
$0.1 \times \sqrt{18/2}$

$0.1 \times \sqrt{200/2}$



Disc diameter (m)	Flow rate (ml s^{-1})	Avg. film thickness (μm)	Residence time (s)	Heat transfer coefficient in film (kW m^{-2} K^{-1})
0.1	2	68.9	0.270	52
0.3	18	68.9	0.270	52
1.0	200	68.9	0.270	52

Variable conversion[2]



	Disc diameter (m)	Disc speed (rpm)	Throughput (cm^3/s)	Mean disc residence time (s)[a]	Film thickness at disc edge (μm)[a]	Surface area per unit volume (m^2/m^3)
Lab-scale SDR	0.2	400	20	0.2	82	8200
Industrial-scale SDR	1	127	50	2.0	82	8200

$\times\sqrt{2.5 \cdot 10}$ $\quad \times {}^{1}/_{\sqrt{10}}$ $\quad \frac{Q_{plant}}{Q_{lab}} = 2.5$ $\quad f = 10$

---

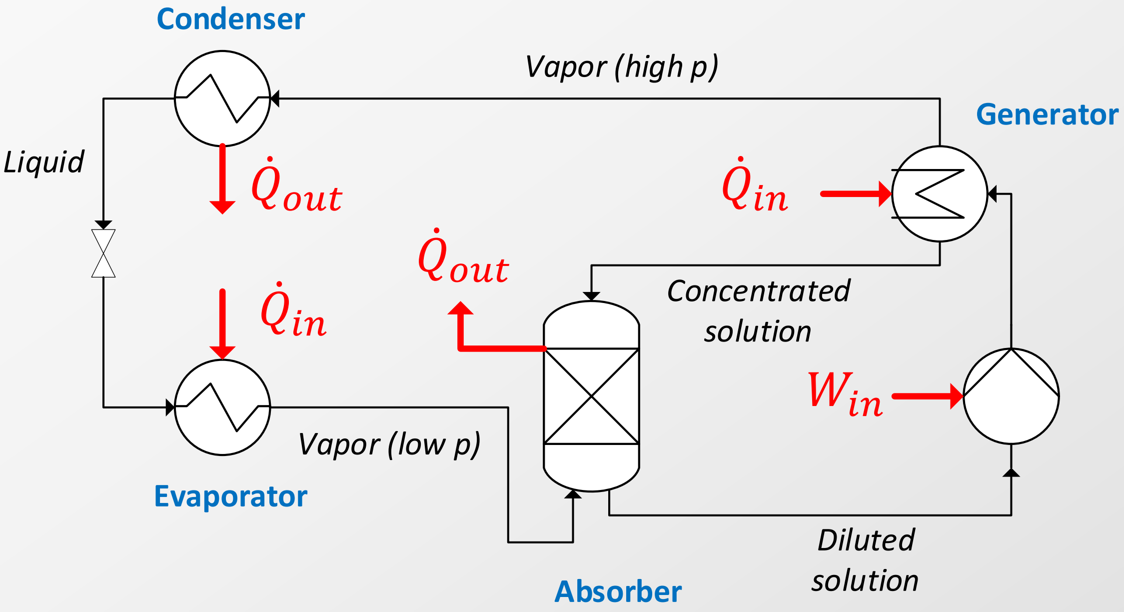
[1] *Pask et al., Polym. Chem., 2012, 3, 2698–2707*

[2] *Boodhoo, K., Spinning Disc Reactor for Green Processing and Synthesis, in Process Intensification for Green Chemistry, Wiley, 2013, 59–90.*

Absorption refrigeration systems

Principle of absorption refrigerator

Environmental concerns over the use of Global Warming Potential refrigerants ⇨ increased efforts in sorption cooling technology (absorption and adsorption cooling), which **does not use CFCs**. Current absorbents include aqueous LiBr and aqueous NH_3 (toxic)



Basic absorption cooling cycle

Vapor compression vs absorption cooling

Vapor compression

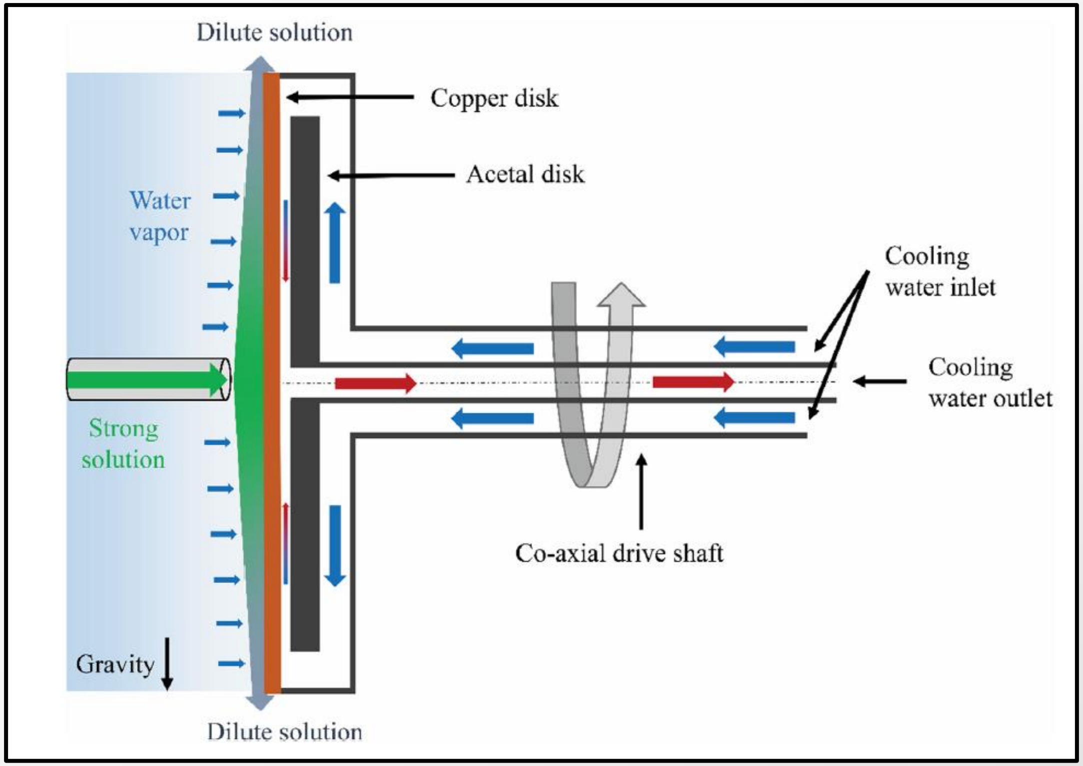
- Compression / expansion cycle
- Compression involves electrically-driven compressor

Absorption cooling

- Compressor replaced by chemical cycle (absorption / desorption)
- Much less work input required for pumping absorbent than for compressing vapor
- Generator: heat input required to evaporate the refrigerant vapor out of the solution
- Uses a source of heat to produce cold
- Useful sink of waste heat or solar energy

Absorption refrigeration systems

Use of a spinning disk absorber



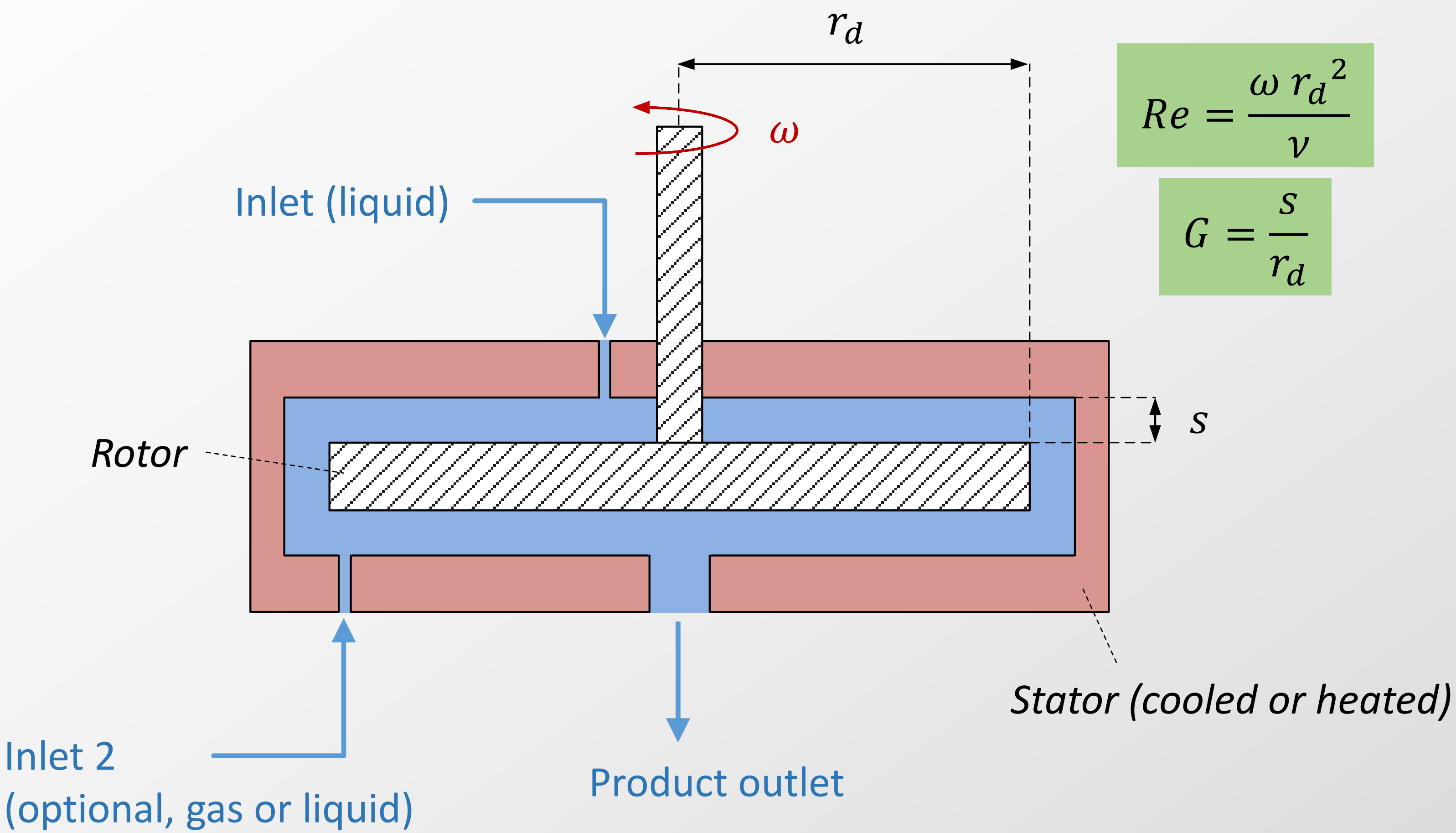
- Absorption <u>and</u> heat transfer intensified → potentially cheaper absorption chillers.
- Spinning disk absorbers enable the use of a new generation of absorbents with higher viscosity than aqueous lithium bromide (current absorbent)

Bangerth et al., international Journal of Heat and Mass Transfer 129 (2019) 326–341

2.2 Spinning disk reactors

2.2.2 Rotor-stator spinning disk reactor (RS-SDR)

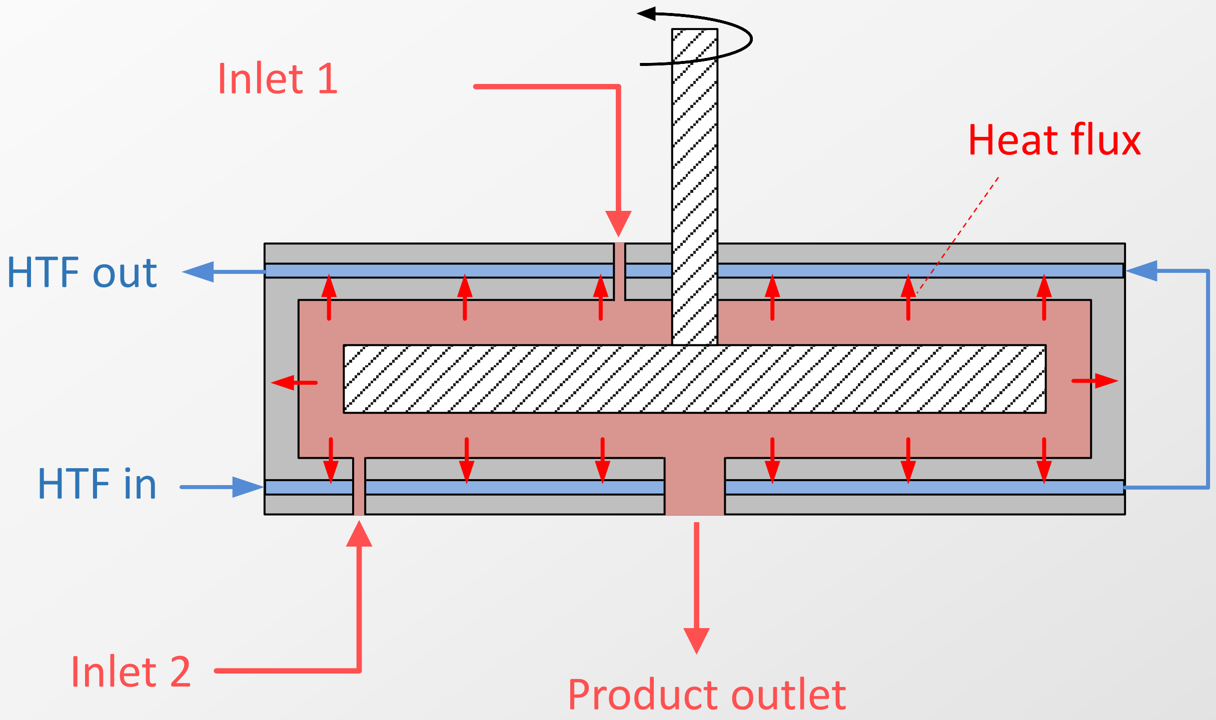
RS-SDR principle



$$Re = \frac{\omega \, r_d{}^2}{\nu}$$

$$G = \frac{s}{r_d}$$

Heat transfer in RS-SDR



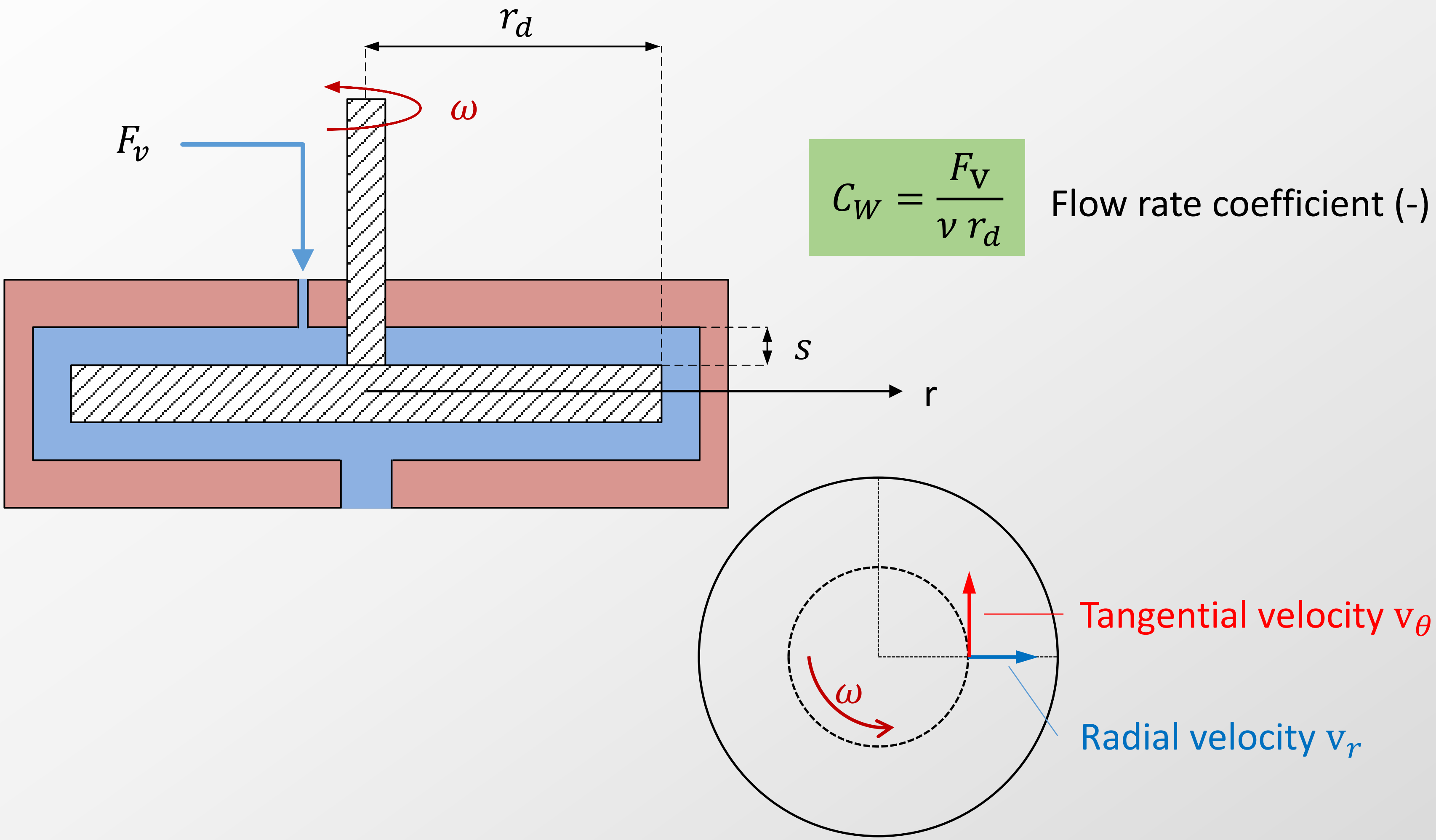
RS-SDR specifics

- Rotating disc enclosed in cylindrical housing
- Short gap between rotor and stator ($s \sim 1mm$)
- High velocity gradient in gap → high shear force
    - Rotational speed ~1000-4500 rpm
    - Increase of gas-liquid or liquid/liquid interfacial area
    - Increased turbulence
    - ⇨ Enhanced mass and heat transfer rates
- High cooling/heating capacity
- Plug-flow close to rotor axis but significant extent of backmixing in rotor rim zone
- Multiple rotors can be stacked on same shaft

RS-SDR performance

- Mean residence time
  - $V \sim 100$ ml for 25-cm disk with $s = 1$mm
    → τ = 1-60 s for F_V = 6 – 360 l/h
- Mixing time
  - $\tau_{mx} = 0.1 – 10$ ms
- Heat transfer
  - $U = 10\text{-}50$ kW/m^2 K
  - $A = 0.1$ m^2 for 25 cm disk
- Mass transfer
  - $k_{LG} = 10^{-3} - 10^{-2}$ m/s
  - $a_{LG} = 100$ m^{-1}
  - $k_{LS} = 10^{-3}$ m/s
  - $a_{LS} = 1000$ m^{-1}

Flow structure in RS-SDR



$$C_W = \frac{F_V}{\nu\, r_d}$$

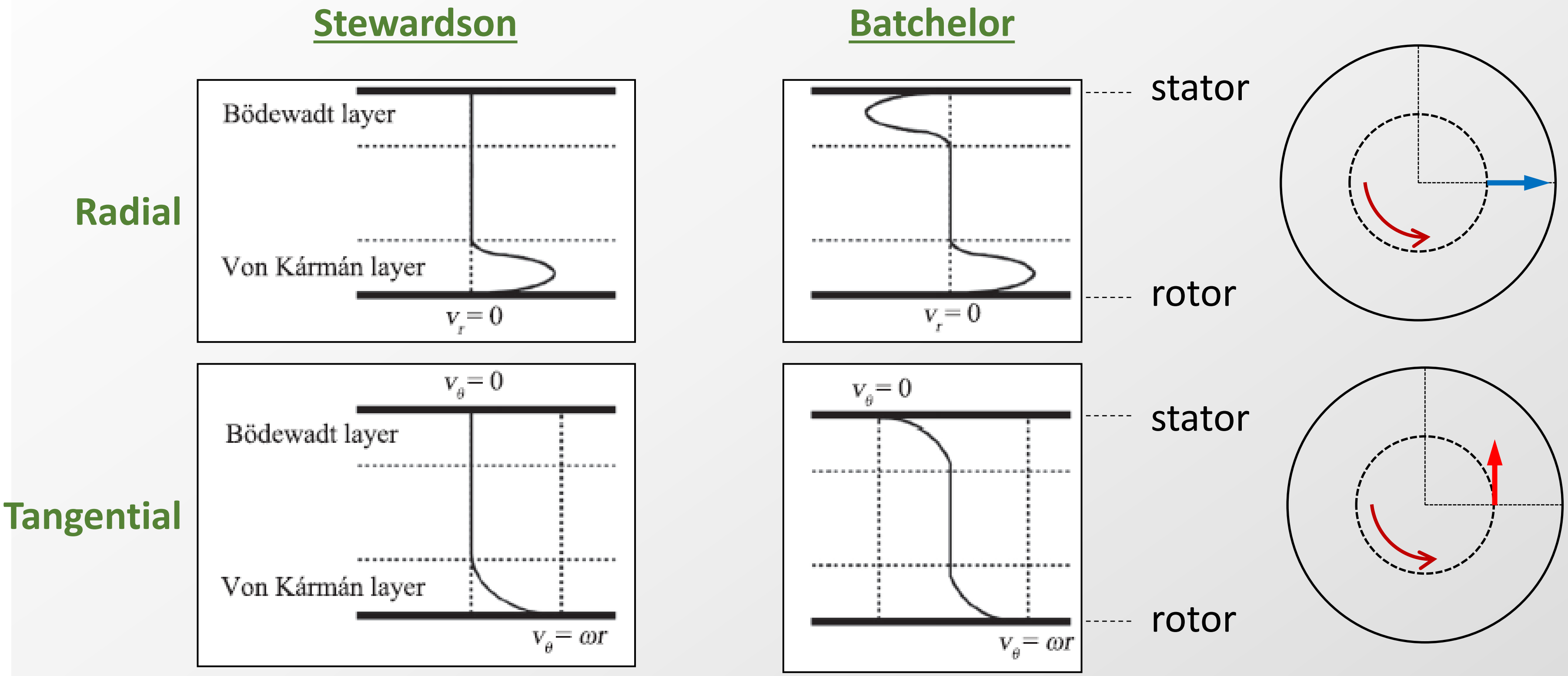
Flow rate coefficient (-)

Optional

Flow structure in RS-SDR

Schematic radial and tangential velocity profiles

Without throughflow $(F_V = 0)$



Stewardson

Batchelor

Radial

Tangential

stator

rotor

stator

rotor

Low radial positions → r **High radial positions**

M.M. de Beer et al., Chemical Engineering Journal 242 (2014) 53–61

Flow structure in RS-SDR

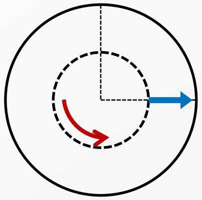
Schematic radial and tangential velocity profiles for a net throughflow $(F_V > 0)$

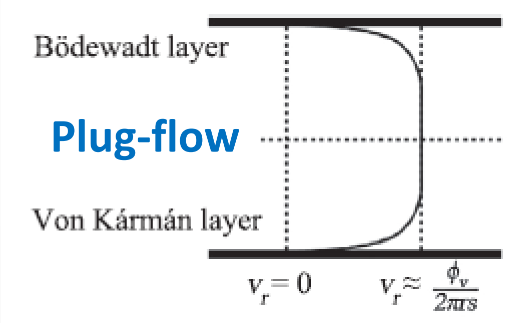
$F_V \longleftrightarrow \omega$

Troughflow governed

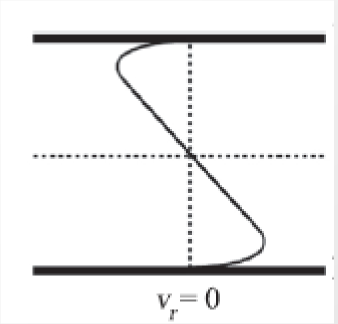
Rotation governed
(torsional Couette flow)

Radial





Plug-flow

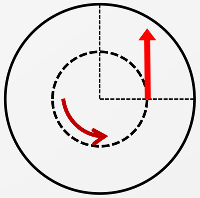


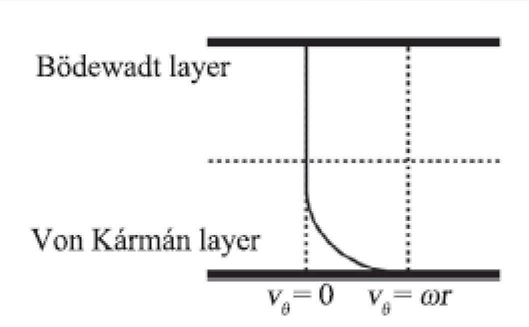
stator

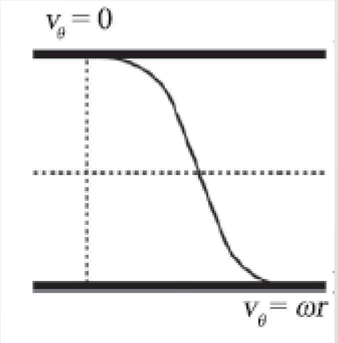
← **Back-mixing**

rotor

Tangential





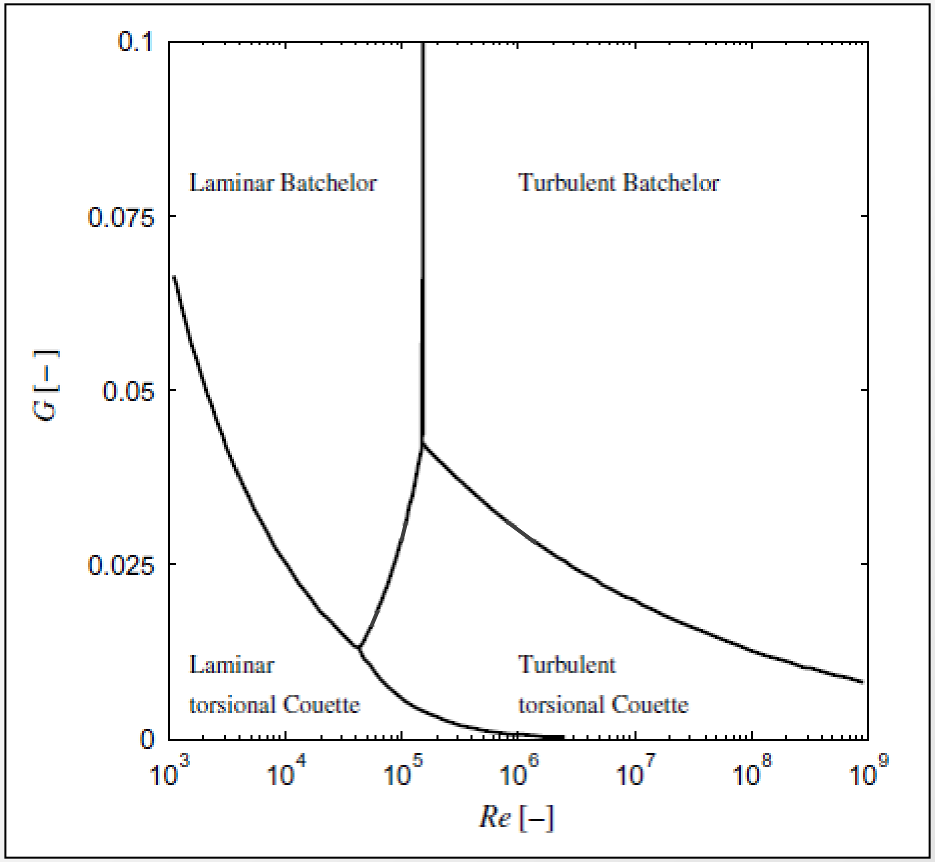


stator

rotor

Low radial positions ⟶ r **High radial positions**

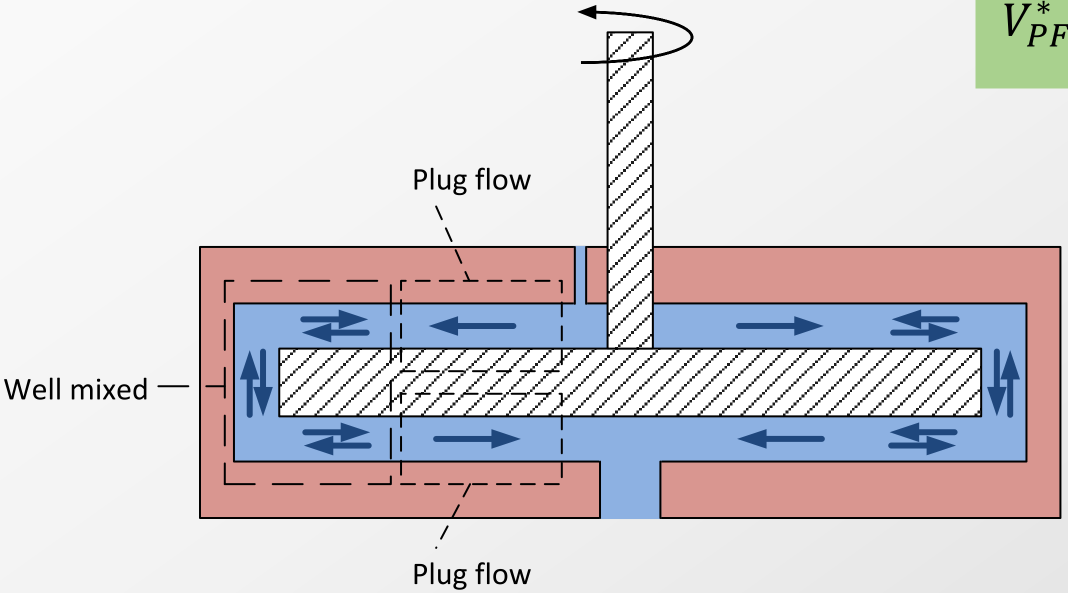
Flow regimes in RS-SDR



Separated layers = Batchelor
Merged boundary layers=torsional Couette
Both flow structures can be laminar or turbulent

RTD in RS-SDR

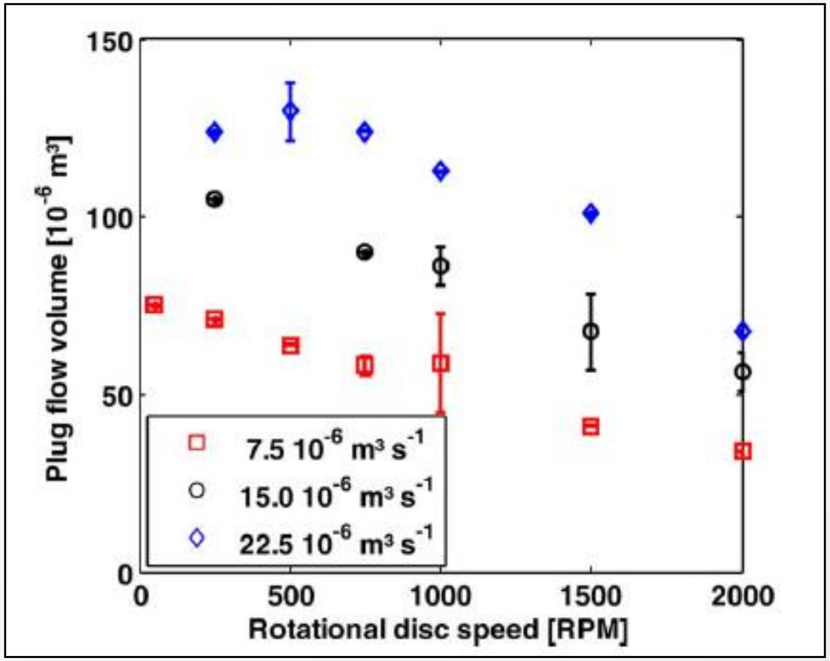
$$V_{PFR}^{*} = \frac{V_{PFR}}{V_r}$$



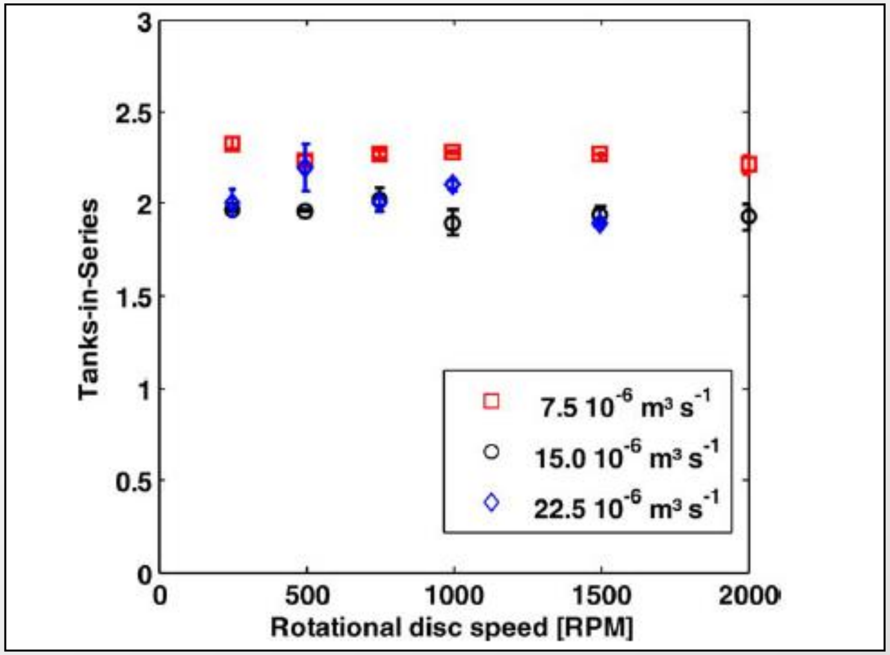
RTD can be modelled in using a combination of plug flow and well-mixed regions

RTD in RS-SDR

Plug flow region



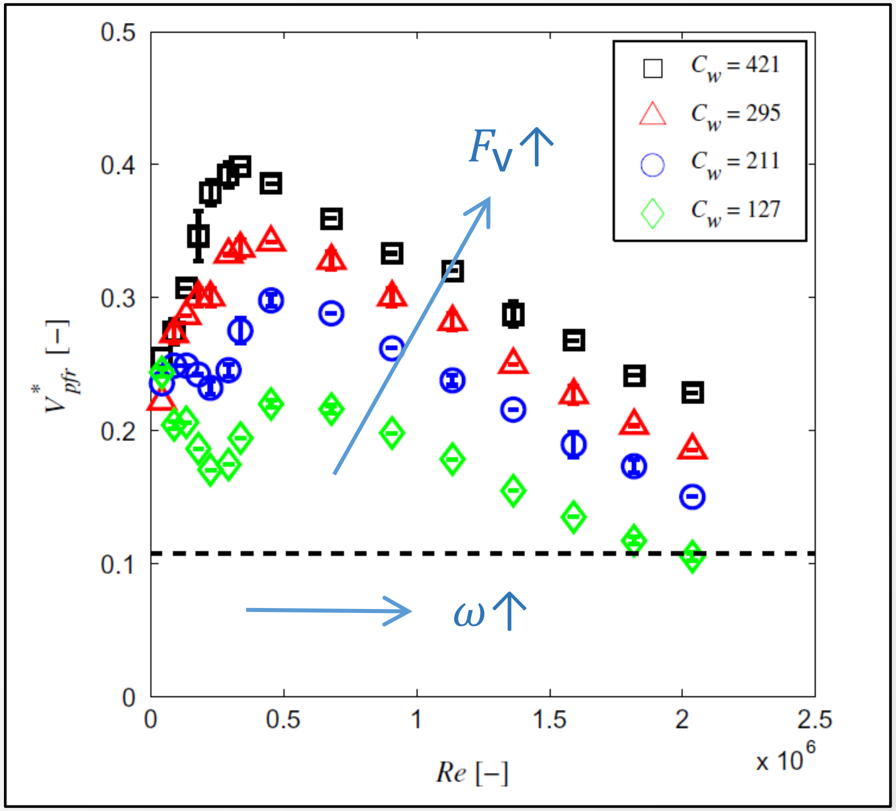
Well-mixed region



RTD modelled using a plug-flow combined to a well-mixed region corresponding to 2-3 ideal CSTRs, depending on conditions (ω and F_V)

Visscher et al., AIChE Journal (2013) Vol. 59, No. 7, 2686-2693

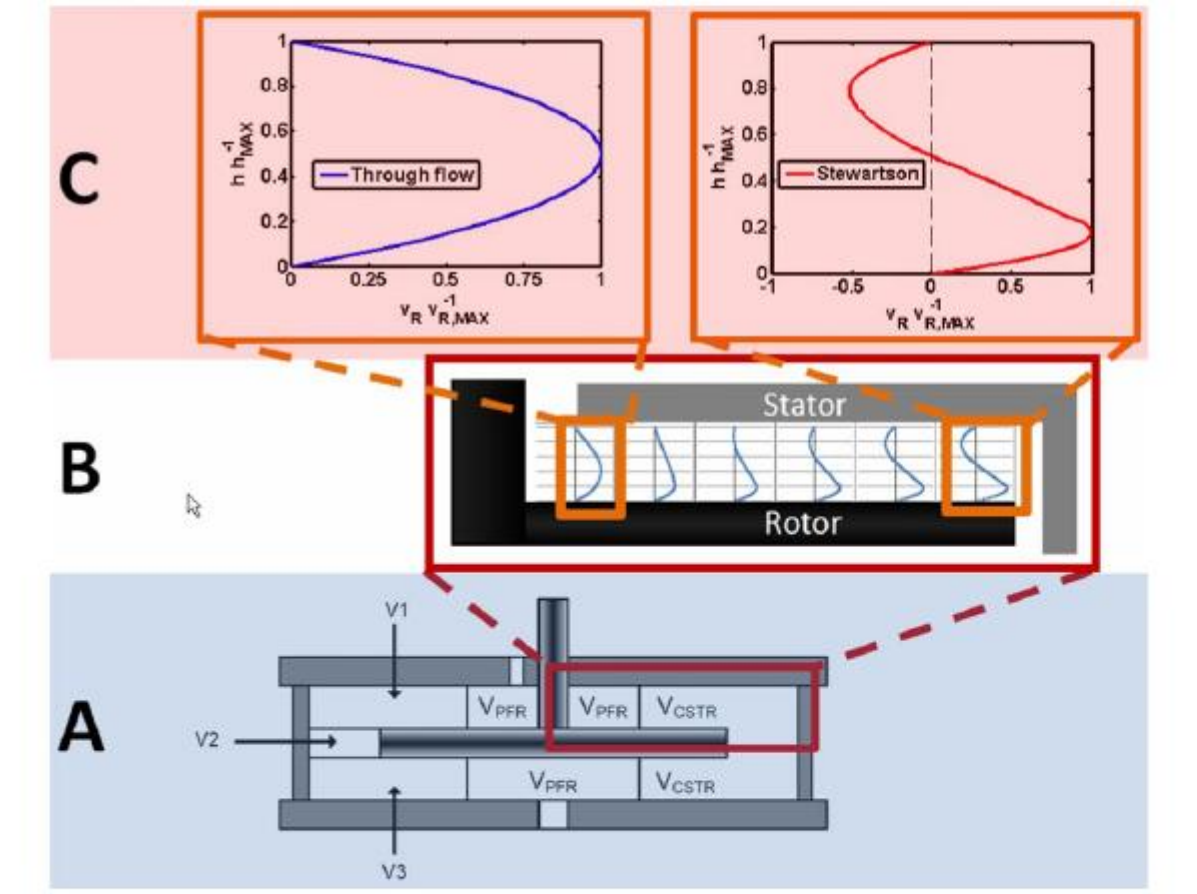
RTD in RS-SDR



RTD modelled using a plug-flow combined to a well-mixed region corresponding to 3 ideal CSTRs. The relative volumes of the two types of regions depends on ω and F_V i.e., on $Re = \frac{\omega\, r_d^2}{\nu}$ and $C_W = \frac{F_v}{\nu\, r_d}$

M.M. de Beer et al. / Chemical Engineering Journal 242 (2014) 53–61

Effect of flow structure on RTD

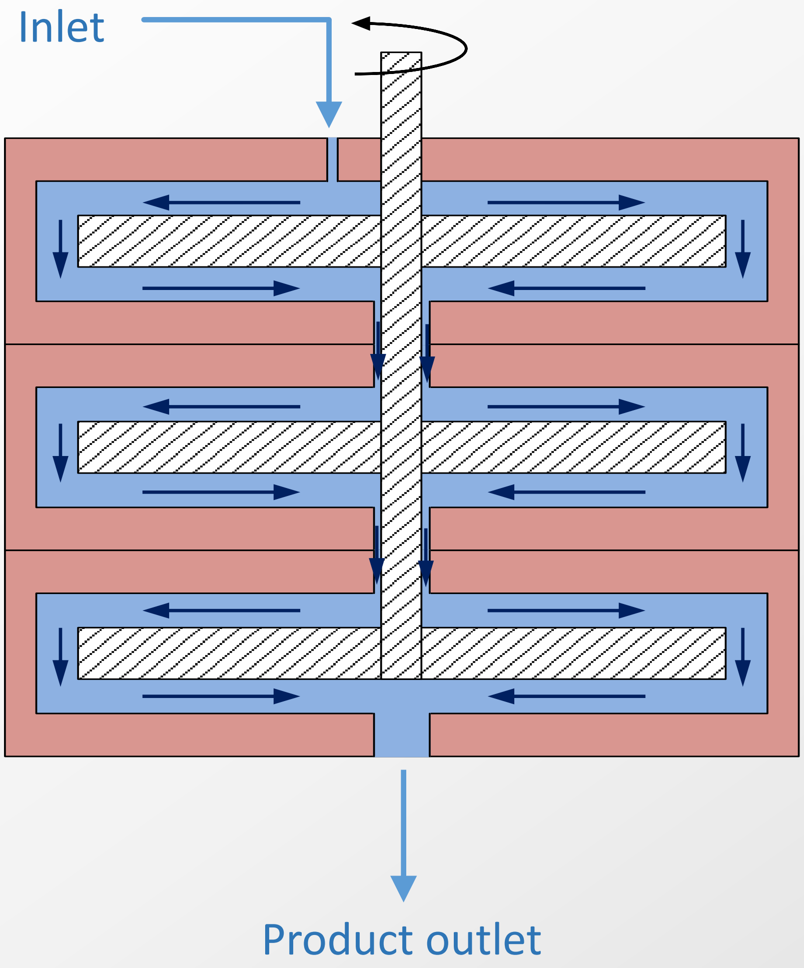


Visscher et al., AIChE Journal (2013) Vol. 59, No. 7, 2686-2693

Effect of flow structure on RTD

- Increase reverse flow in stator boundary layer → increase backmixing → decrease V_{PFR}^*
- Increase ω → stator boundary layer formation closer to rotational axis → decrease V_{PFR}^*
- Higher F_V → increase volume where stator boundary layer suppressed → throughflow dominated → increase V_{PFR}^*

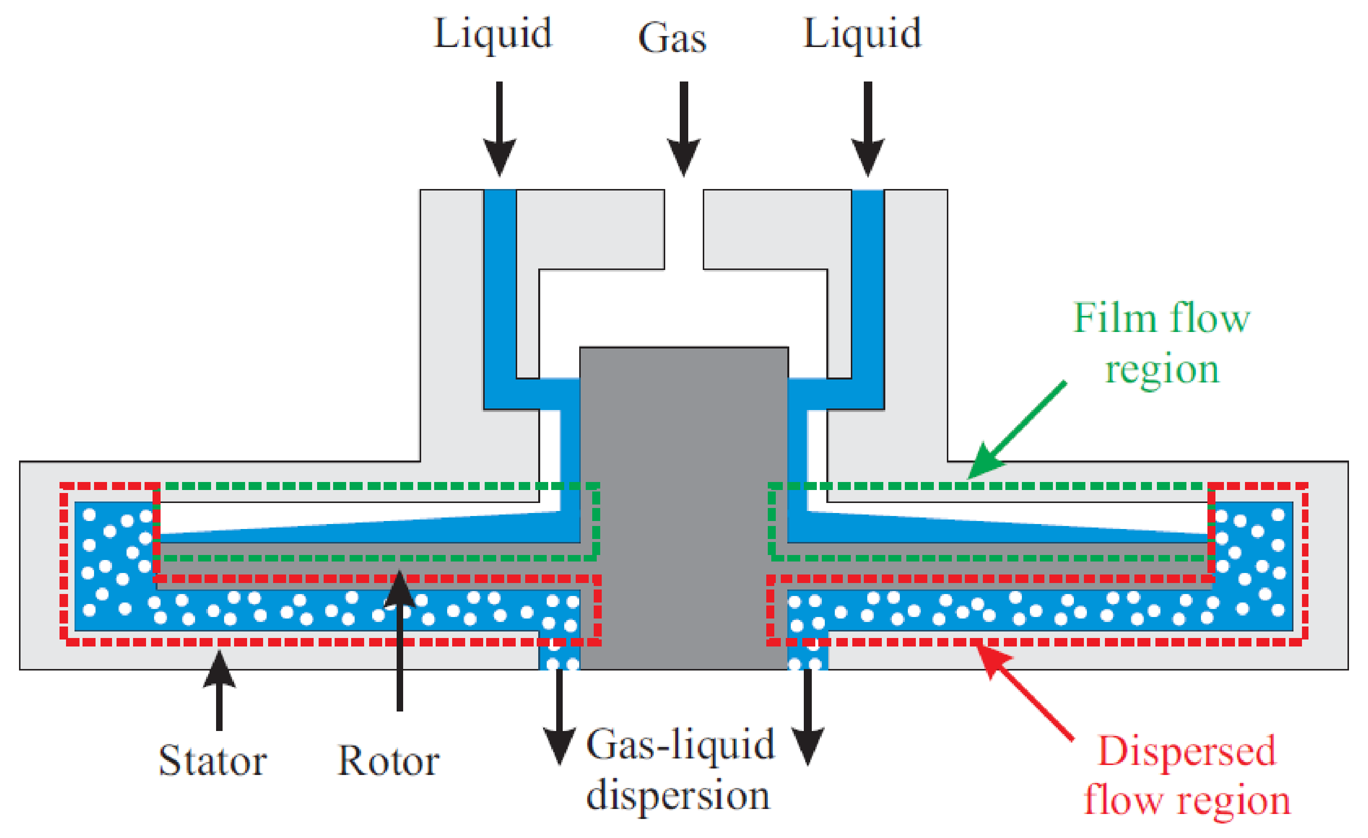
RS-SDR multistage arrangement



Energy dissipation increases faster with disk radius than mass-transfer rate → numbering up better than increasing disk size from an energetic point-of-view*

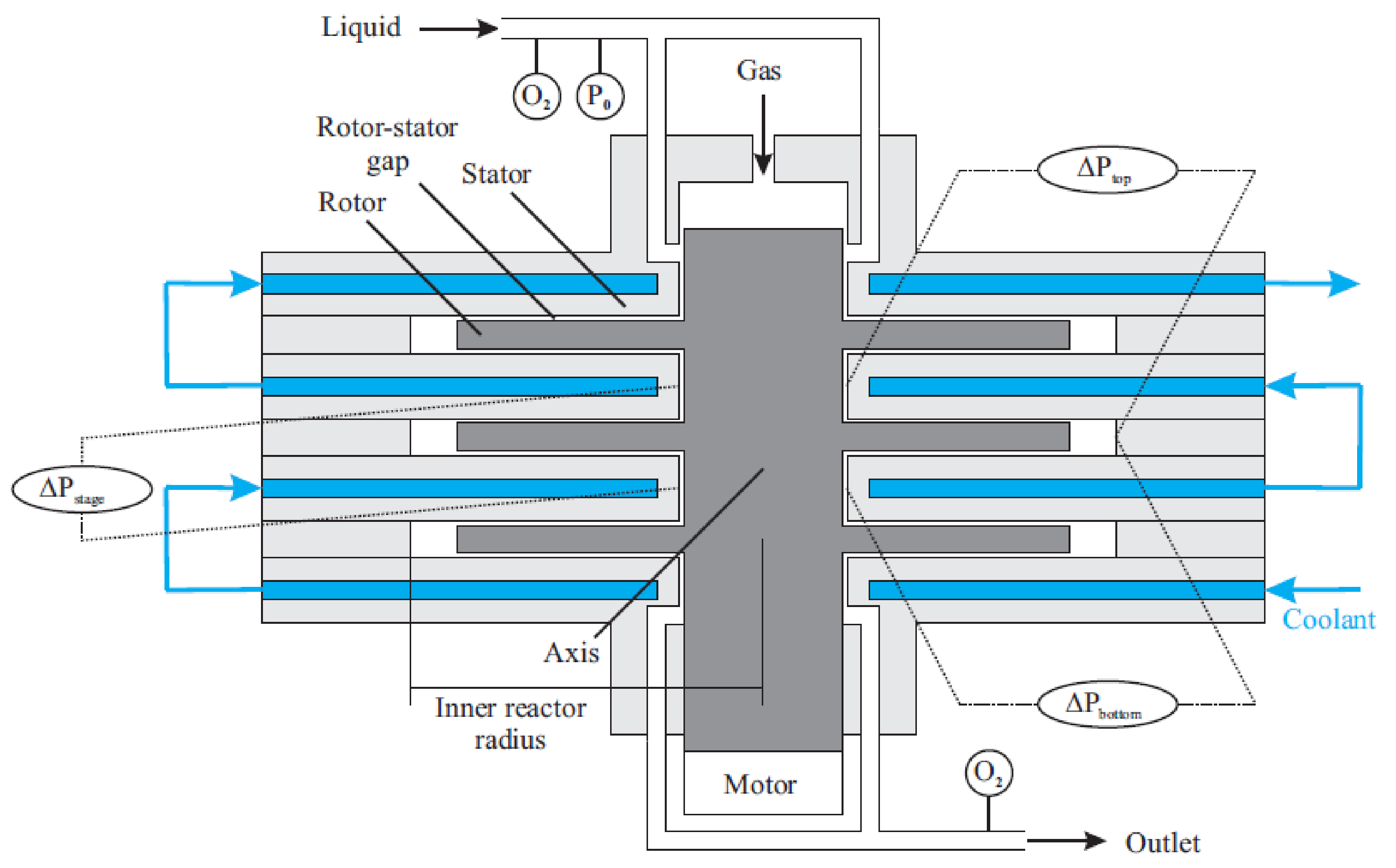
**Meeuwse, et al., AIChE Journal January 2012 Vol. 58, No. 1*

RS-SDR for gas-liquid system



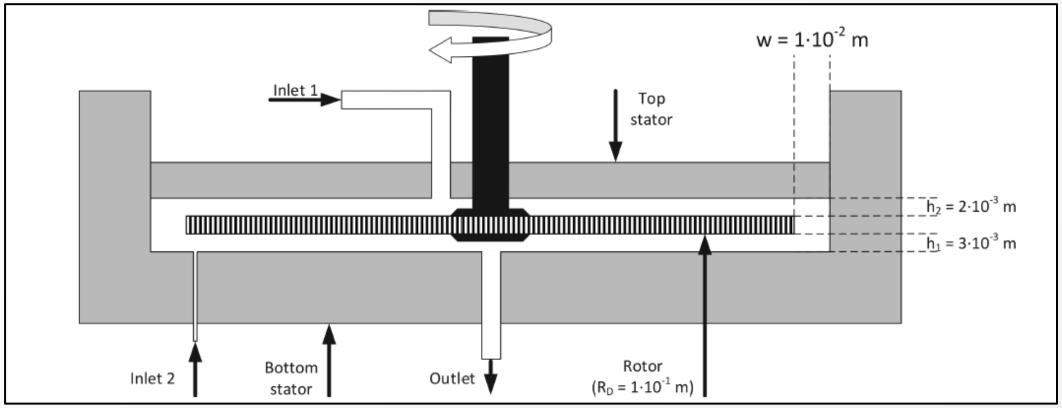
Meeuwse, M. (2011). Rotor-stator spinning disc reactor Eindhoven: Technische Universiteit Eindhoven

Multistage RS-SDR for gas-liquid system

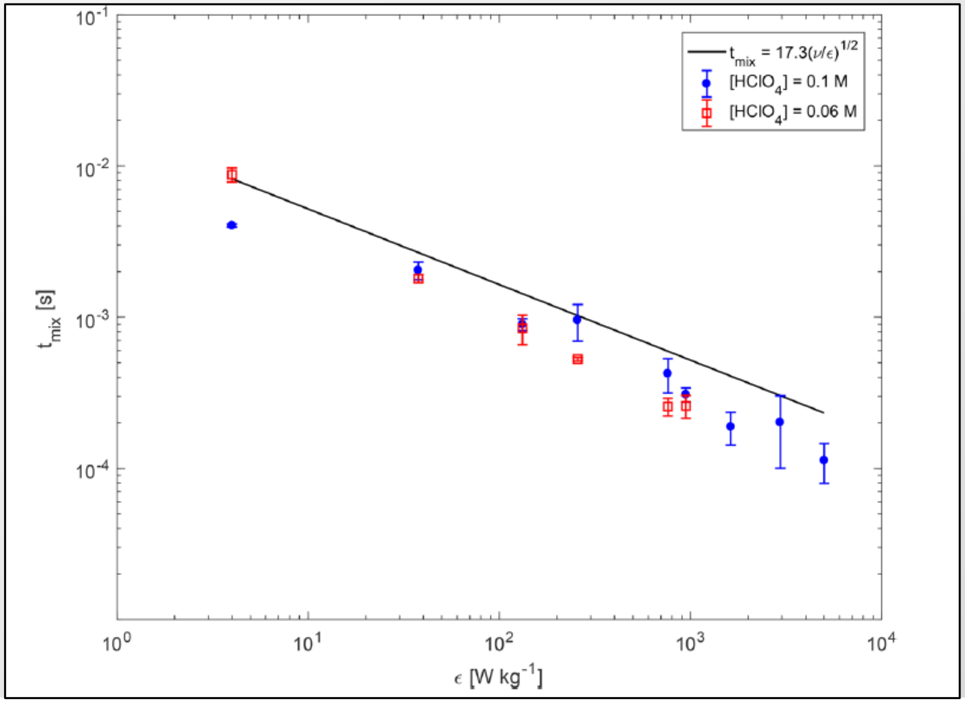


Meeuwse, M. (2011). Rotor-stator spinning disc reactor Eindhoven: Technische Universiteit Eindhoven

RS-SDR mixing time

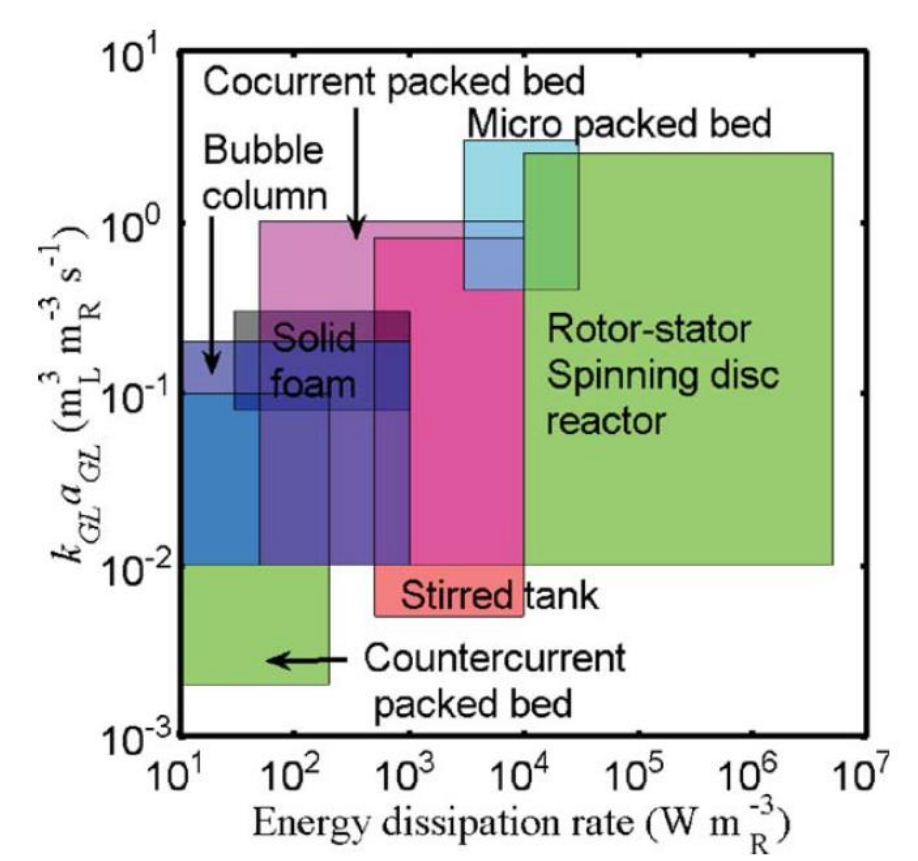


- Mixing time $10^{-4} - 10^{-2}$ s
- Mixing time follows $t_{mx} \propto \varepsilon^{-0.5}$ as for micromixers (see chapter 6)



Martínez et al., Ind. Eng. Chem. Res. 2017, 56, 13454−13460

Mass transfer in RS-SDR vs other reactors



Meeuwse, et al., AIChE Journal January 2012 Vol. 58, No. 1

RS-SDR benefits

- 40-fold increase in gas/liquid mass transfer coefficients compared to conventional bubble columns
- 25-fold increase in liquid/liquid mass transfer coefficients compared to conventional packed columns
- Well suited for fast exothermic reactions

RS-SDR applications

Intensification opportunities

- High mass transfer
- High heat transfer
- Short micromixing times
- Low reactor volume

- Fast exothermic reactions
    - Faster heat removal
    - Less hot spots due to fast mixing
- Significant safety issues (e.g., product thermal instabilities)
- Mass transfer limitations (multiphase systems, L/L, L/G and combinations

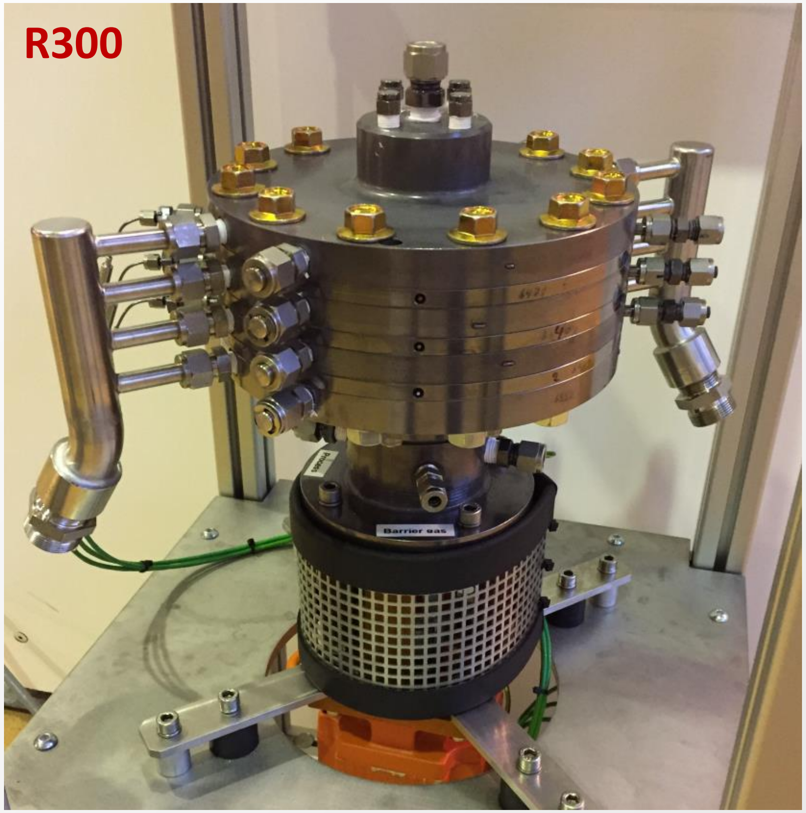
RS-SDR applications

Some relevant applications

- Nitrations, sulfonations, Darzens reaction
- Organometallic reactions (e.g., Li- exchange)
- Chlorination (Cl_2)
- Emulsion polymerization (high viscosity $> 20\ Pa \cdot s$)
- Emulsification
- Precipitation
- Liquid-liquid extraction

Commercial system

Flowid reactor



Reproduced with permission from Flowid

	SpinPro R10	SpinPro R300
Number of stages:	3	3
Temperature:	-20 to 160 °C	-50 to 160 °C
Pressure:	up to 10 bar (g)	up to 10 bar (g)
Reactor volume:	19 ml	135 or 230 ml
Gap size:	0.5 mm	1 or 2 mm
Body material:	SiC	SS316 / Hastelloy C / Tantalum
Seal	None; magnetic drive	Mechanical or triple lip
O-ring material	FFKM	FFKM
Rotation:	up to 8000 RPM	up to 3000 RPM
Max flowrate		600 l/h

Successful scaleup examples

Flowid reactor

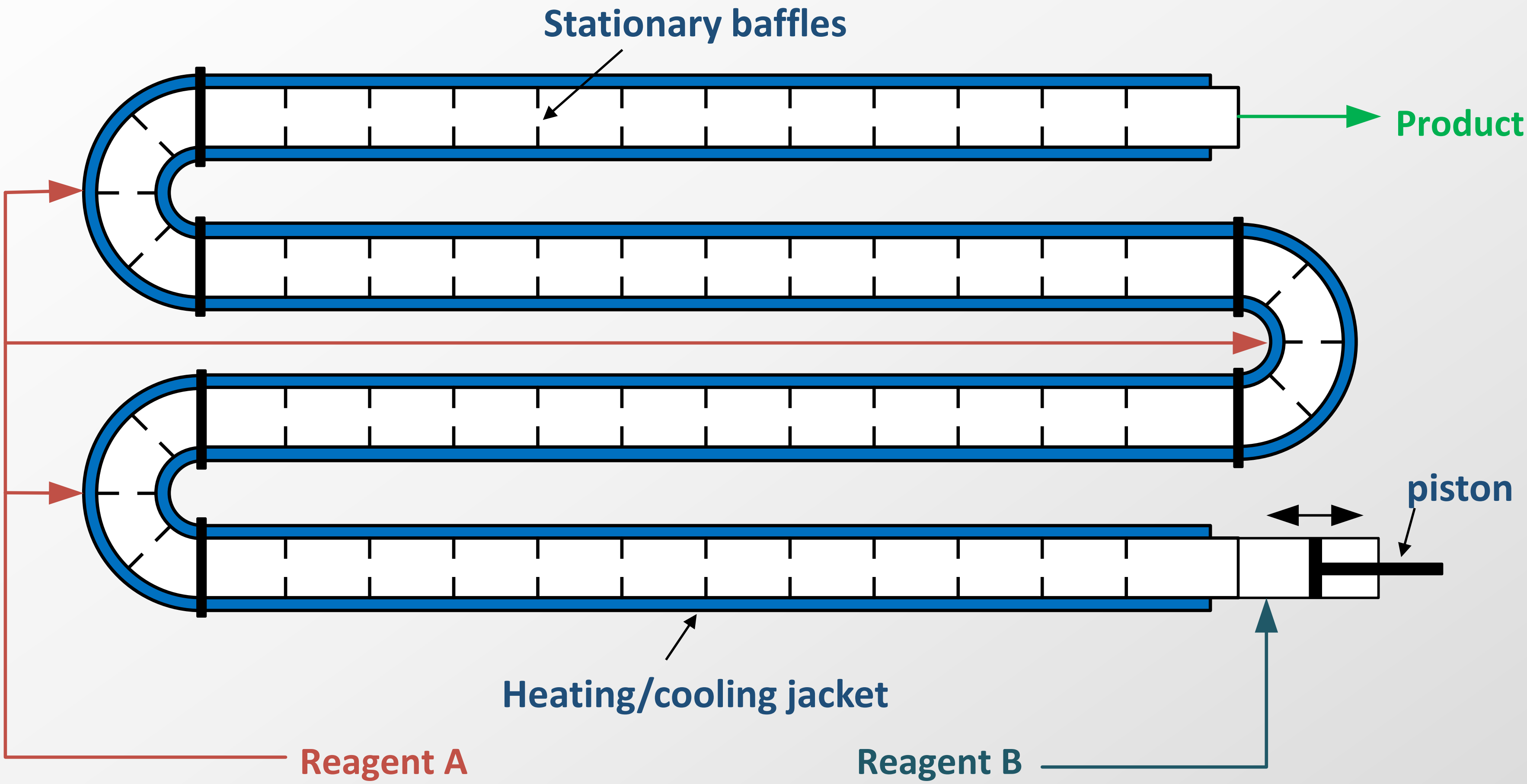
- Halogenation (Cl_2)
- Emulsion polymerization (high viscosity 23 Pa*s)
- Emulsification
- Lithium exchange (BuLi)
- Nitration

2.3 Continuous oscillatory baffled reactors

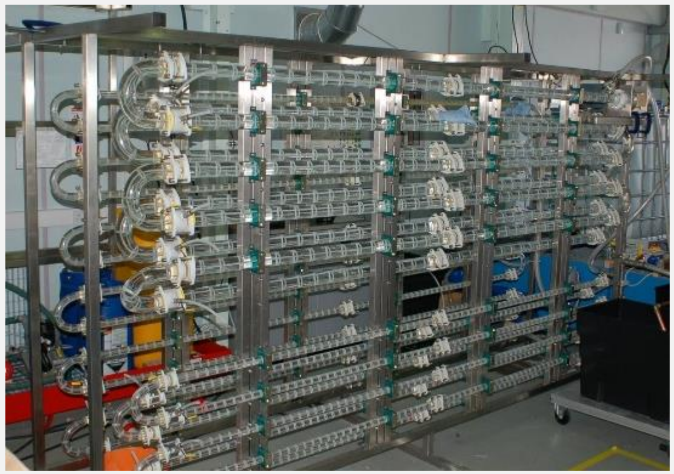
2.3 Continuous oscillatory baffled reactors

2.3.1 Fundamentals of COBRs

Schematic of COBR

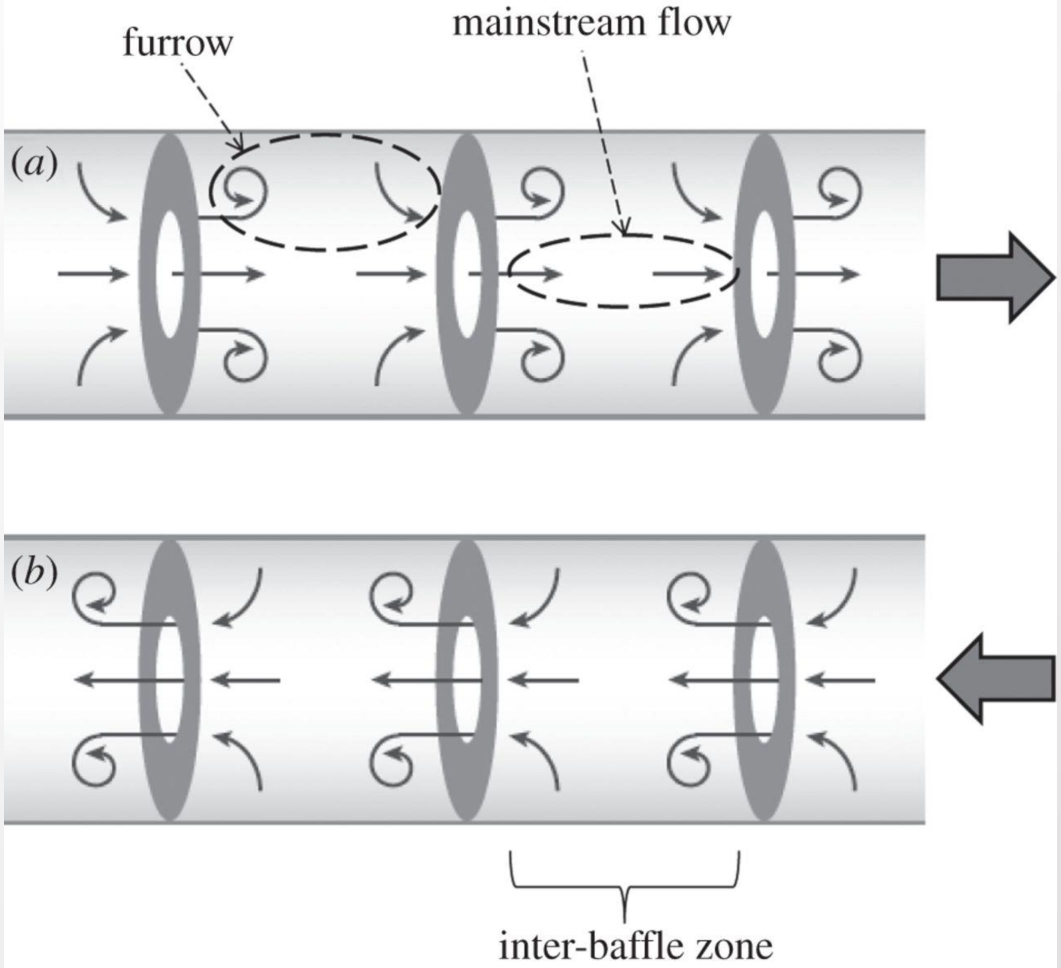


Pictures of COBRs



McGlone et al., Org. Process Res. Dev. 2015, 19, 1186−1202

COBR mixing principle

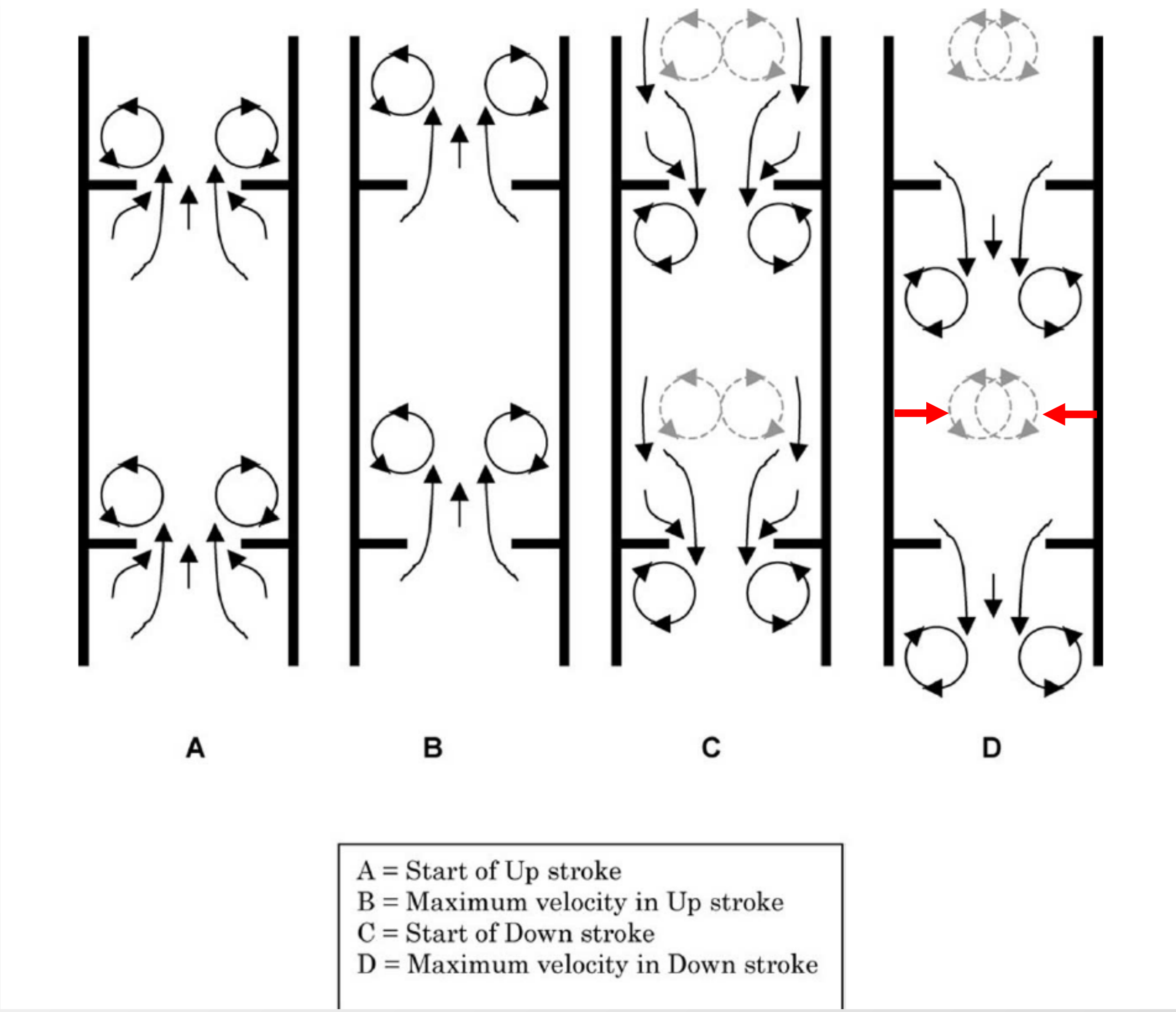


Upstroke

Downstroke

Abbott et al., Biological processing in oscillatory baffled reactors: operation, advantages and potential. Interface Focus 2013, 3.

COBR mixing principle



A = Start of Up stroke
B = Maximum velocity in Up stroke
C = Start of Down stroke
D = Maximum velocity in Down stroke

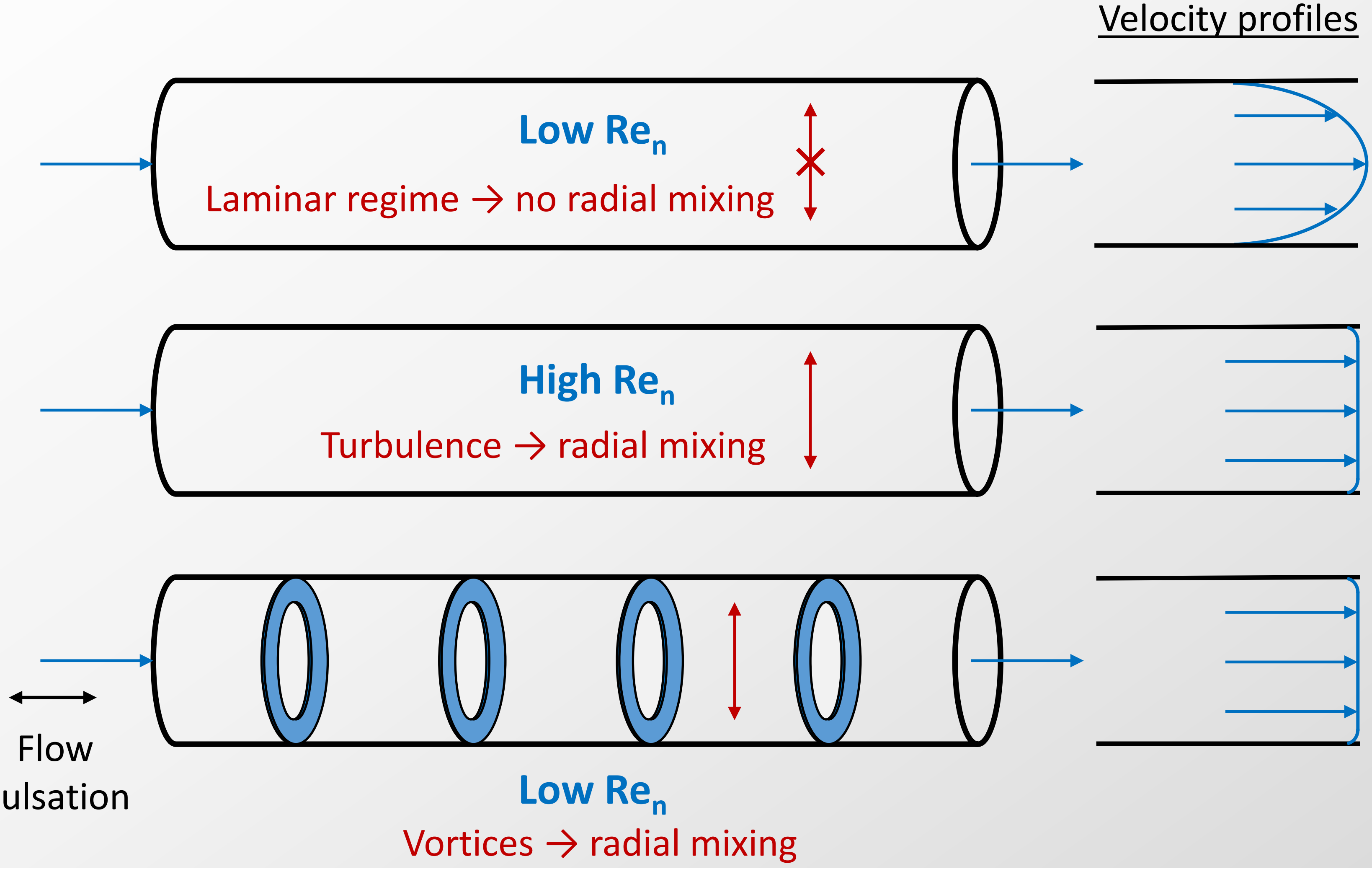
Radial mixing

Jian and Ni, Chemical Engineering Research and Design 2005, 83(10), 1163–1170

COBR features

- Tubular reactor with equally spaced baffles (typically orifice baffles)
- Superimposition of oscillatory flow onto net flow
- Mixing provided by generation and dissipation of eddies (toroidal vortices) formed when flow interacts with baffles
  - ✓High mass and heat transfer
  - ✓Radial mixing
- Mixing decoupled from net flow
  - ✓Low axial dispersion achievable even at low net flowrates (i.e. at low Re_n)

Velocity profile in tubular reactors vs COBR



Velocity profiles

Low Re_n

Laminar regime → no radial mixing

High Re_n

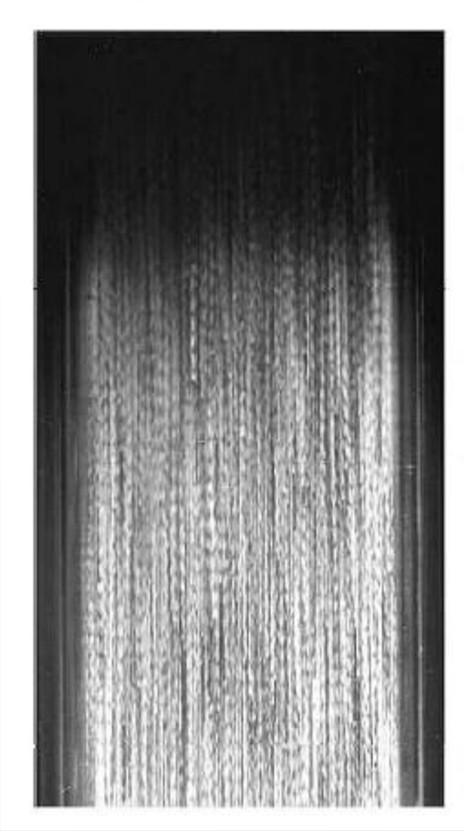
Turbulence → radial mixing

Flow pulsation

Low Re_n

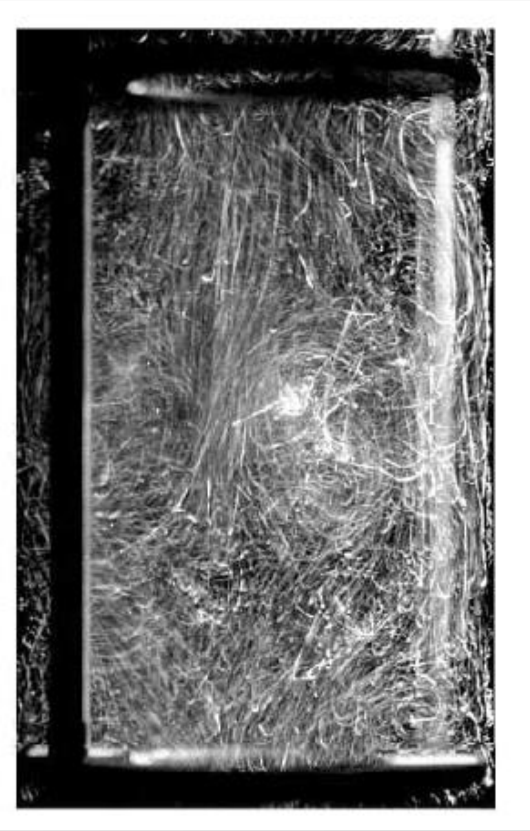
Vortices → radial mixing

Flow visualization in COBR



Tube w/o baffles
→no benefit of oscillations

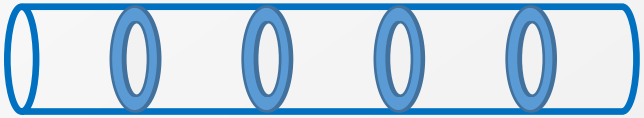
COBR low Re_o
(“soft” mixing)



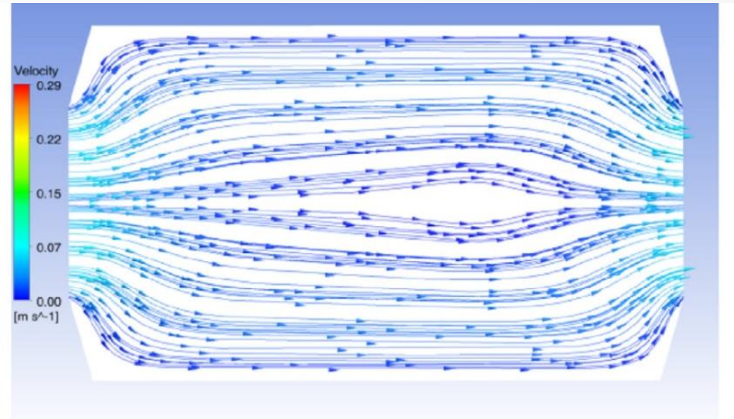
COBR high Re_o
(turbulent-like)

Ni et al., Trans IChemE, Vol 81, Part A, March 2003

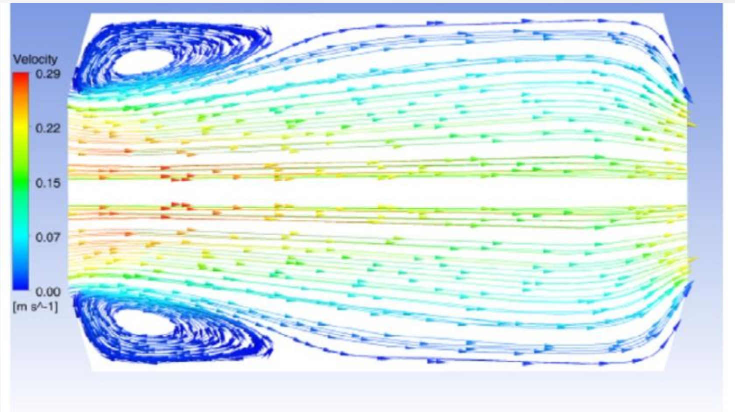
Streamlines (CFD) for single orifice baffle configuration



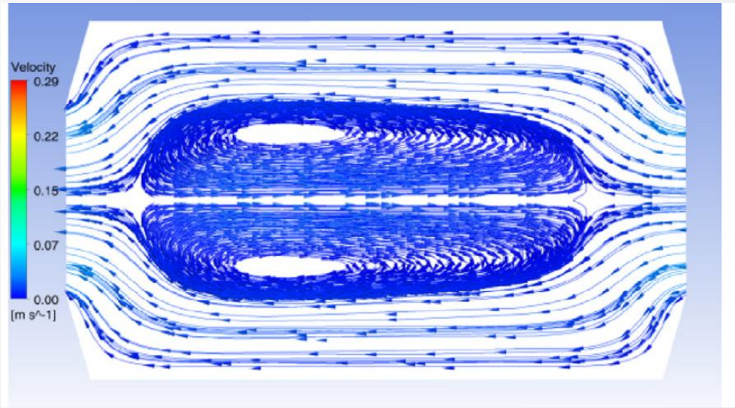
t/T=0



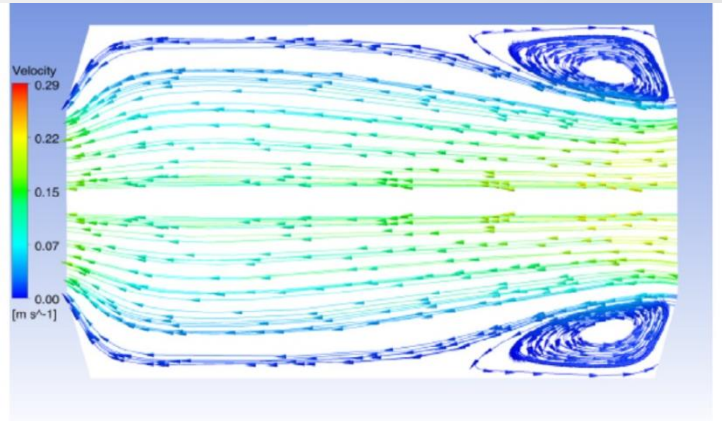
t/T=0.25



t/T=0.5



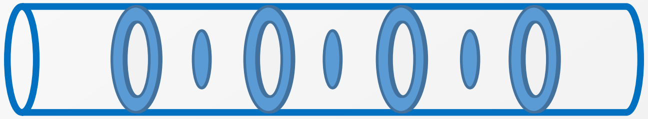
t/T=0.75



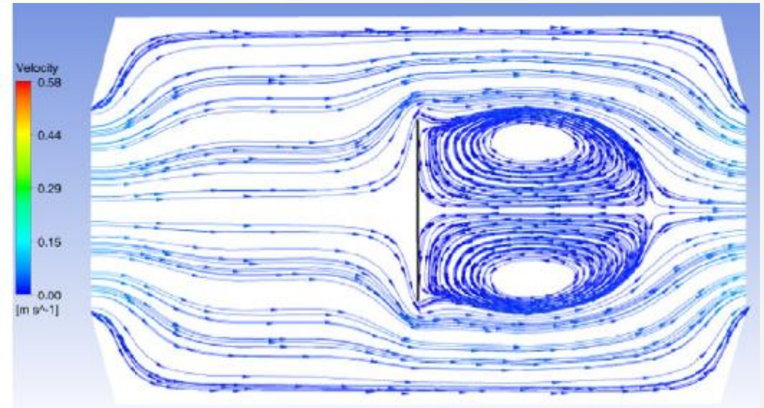
Mazubert et al., Chemical Engineering and Processing 108 (2016) 78–92

f = 1.05 Hz, A = 16.5 mm, u_{net} = 14.05 mm/s. T: oscillation period

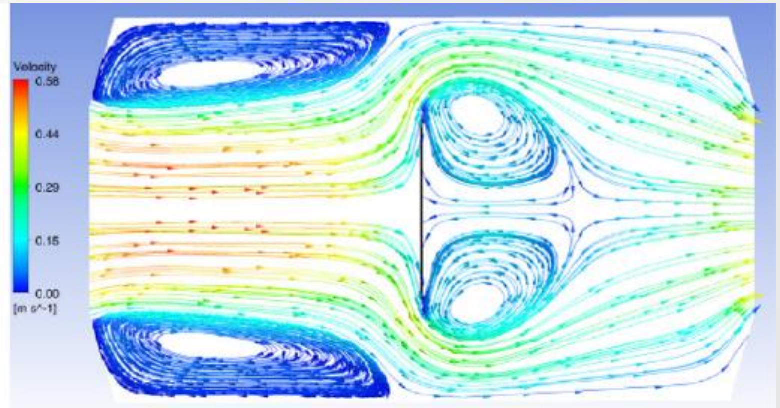
Streamlines (CFD) for disk-and-donut configuration



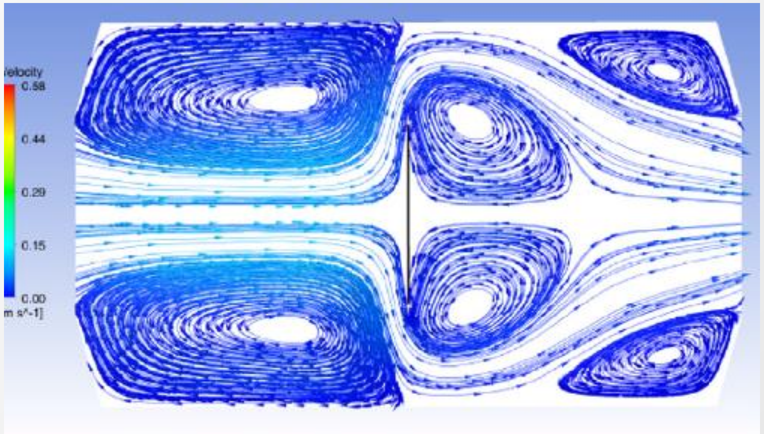
t/T=0



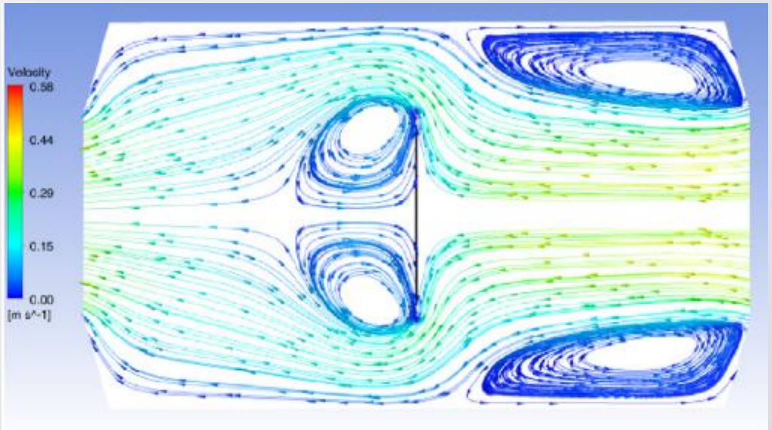
t/T=0.25



t/T=0.5



t/T=0.75



Mazubert et al., Chemical Engineering and Processing 108 (2016) 78–92

f = 1.05 Hz, A = 16.5 mm, u_{net} = 14.05 mm/s. T: oscillation period

Pressure drop and energy dissipation for various baffle designs

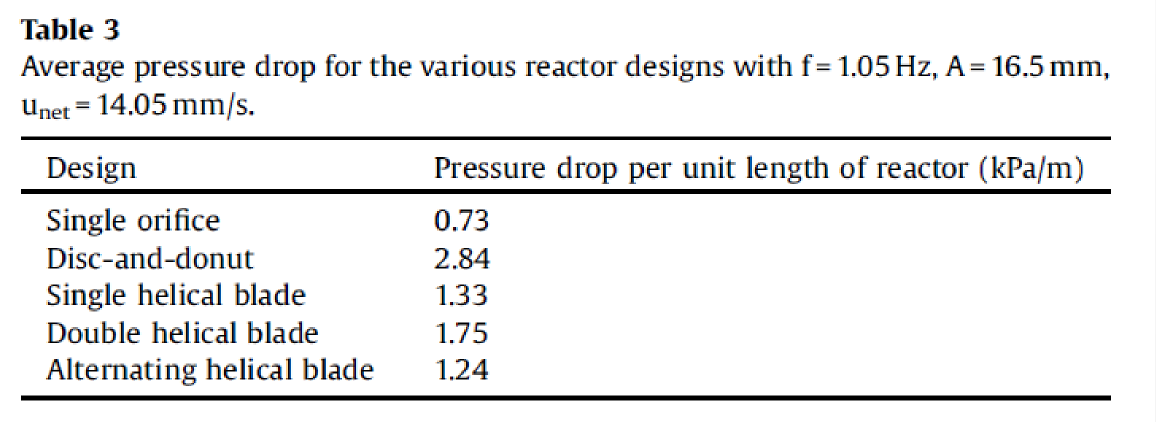


Table 3
Average pressure drop for the various reactor designs with f = 1.05 Hz, A = 16.5 mm, u_{net} = 14.05 mm/s.

Design	Pressure drop per unit length of reactor (kPa/m)
Single orifice	0.73
Disc-and-donut	2.84
Single helical blade	1.33
Double helical blade	1.75
Alternating helical blade	1.24

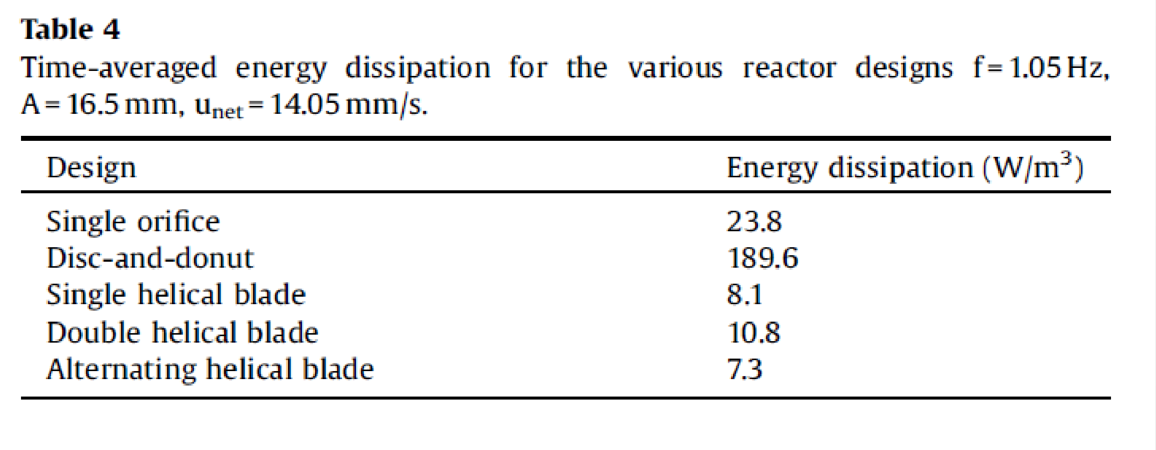


Table 4
Time-averaged energy dissipation for the various reactor designs f = 1.05 Hz, A = 16.5 mm, u_{net} = 14.05 mm/s.

Design	Energy dissipation (W/m^3)
Single orifice	23.8
Disc-and-donut	189.6
Single helical blade	8.1
Double helical blade	10.8
Alternating helical blade	7.3

Mazubert et al., Chemical Engineering and Processing 108 (2016) 78–92

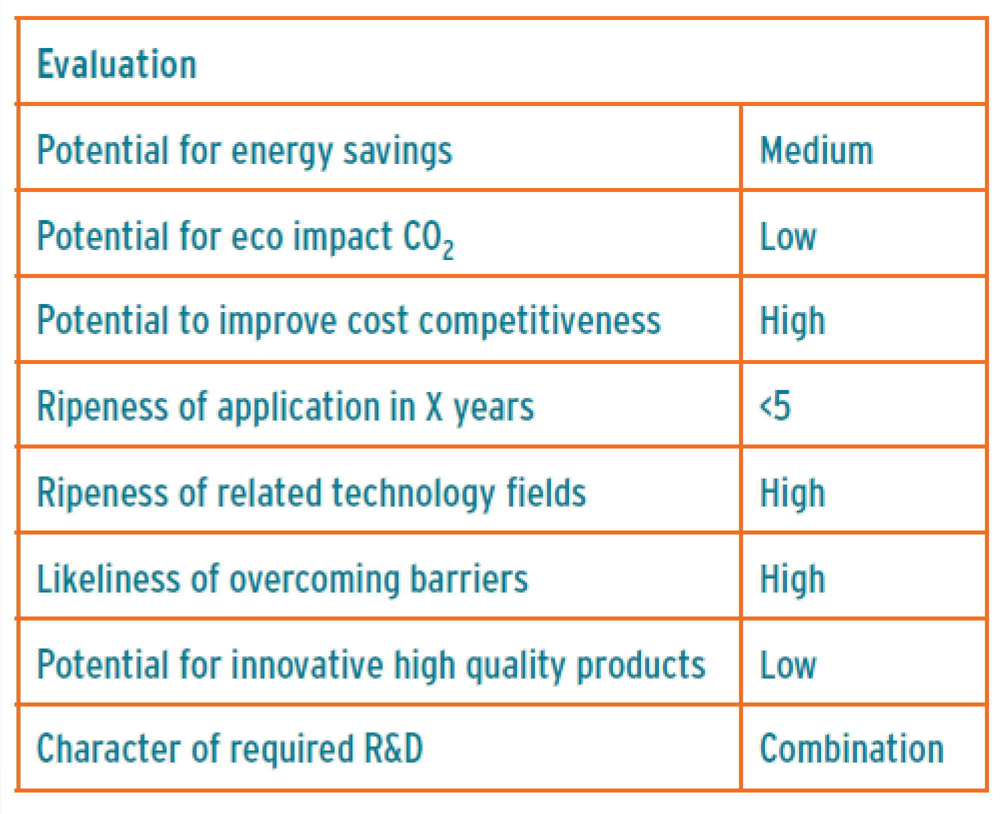
COBR fields of application

- Heat and mass transfer operations
- Liquid-liquid reaction systems
  - High mass & heat transfer rates
- Polymerizations
- Flocculation
- Crystallization
  - Plug flow
  - High heat & mass transfer rates
  - Control of MSZW
- Bioprocessing
  - Low shear rate
  - High mass transfer

COBR limitations

- Gaseous components
  - Pulsation dampening
- High fluid viscosities
- High particle density
  - Settling
- High solid concentration
  - Settling
- “Sticky” solids
  - Fouling

COBR evaluation*



Evaluation	
Potential for energy savings	Medium
Potential for eco impact CO_2	Low
Potential to improve cost competitiveness	High
Ripeness of application in X years	<5
Ripeness of related technology fields	High
Likeliness of overcoming barriers	High
Potential for innovative high quality products	Low
Character of required R&D	Combination

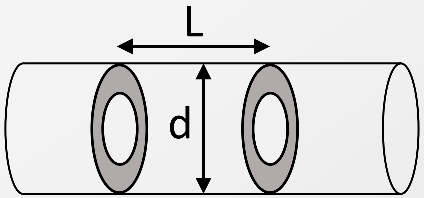
**European roadmap for process intensification, 2009*

2.3 Continuous oscillatory baffled reactors

2.3.2 Characterization and scaleup

Key geometrical parameters

To be kept constant upon scaleup

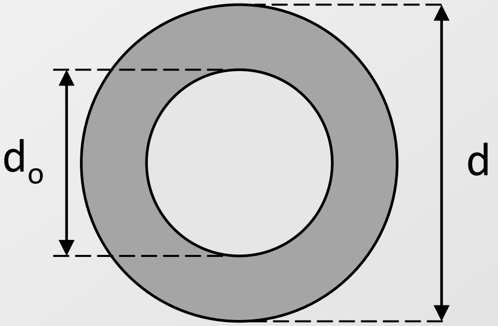


$$\frac{L}{d}$$

Baffle spacing (L) to internal tube diameter (d)

$$\alpha = \left(\frac{d_o}{d_e}\right)^2$$

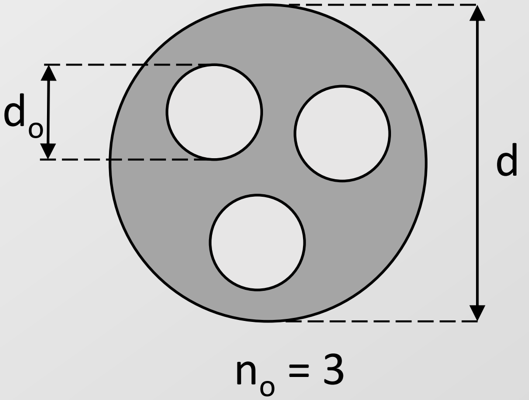
Open cross-sectional area



$$d_e = \sqrt{\frac{d^2}{n_o}}$$

Effective diameter (multi-orifice systems)

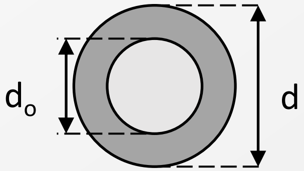
$n_o = 1 \Rightarrow d_e = d$



Optimal L/d

- $\frac{L}{d}$ typically 1 - 3, but **optimal range** based on mass transfer rates and RTD is **1.5 - 1.8**
  - $\frac{L}{d}$ too small: restrained growth of vortices ⇨ reduction of radial motion
  - $\frac{L}{d}$ too big: vortices cannot spread to entire inter-baffle region ⇨ stagnant regions in which vortices lose intensity
- Keep $\frac{L}{d}$ constant upon scaleup

Optimal open cross-sectional area



$$\alpha = \left(\frac{d_o}{d}\right)^2$$

- Baffle cross-sectional area α typically between 10-50%
  - ➢Too low: small eddies, which do not spread into the entire inter-baffle region (neither cross-section nor length of inter-baffle region). Dead zones.
  - ➢Low: eddies spread to the wall, filling entire chamber. Axi-symmetric vortices with no interaction
  - ➢High: interactions between eddies: good mixing and good radial mixing/plug flow characteristics
  - ➢Too high: eddies channel through orifices (move to next chamber), causing axial dispersion. Eddies destroyed by predominant axial motion.
- Baffle cross sectional area α must be kept constant upon scaleup

Key dimensionless numbers

$$Str = \frac{d_e}{\boxed{4\,\pi\,x_o}}$$

Strouhal number*

Stroke length (amplitude)

$$Re_n = \frac{\rho\,u\,d}{\mu}$$

Net flow Reynolds number

Maximum oscillatory velocity

$$Re_o = \frac{\boxed{2\,\pi\,f\,x_o}\,\rho\,d_e}{\mu}$$

Oscillatory Reynolds number

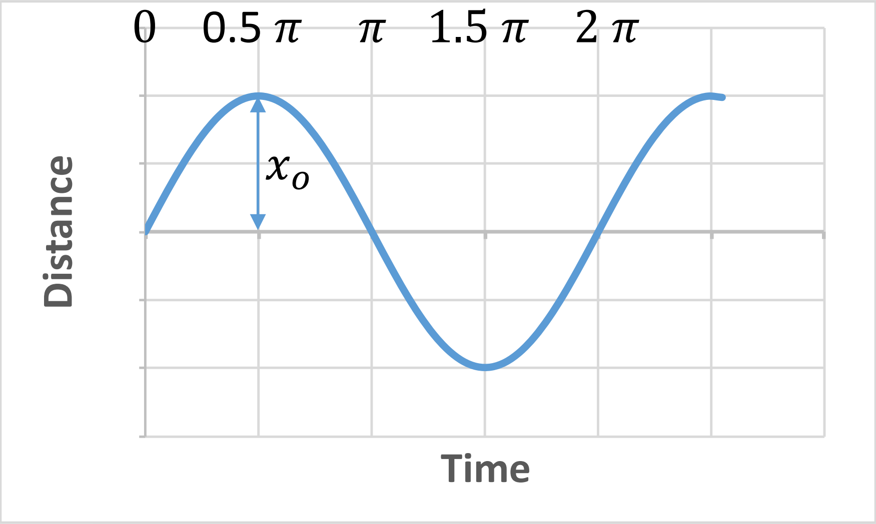
$$\psi = \frac{Re_o}{Re_n}$$

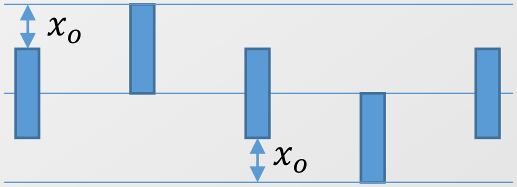
Velocity ratio

Other abbreviations include: St, Sr

Oscillation frequency & amplitude

x_o: center-to-peak amplitude of the oscillation (half of the fluid oscillation distance)





Some considerations on Str, Re_o and ψ

- If Strouhal number Str too low: eddies propagate to adjacent cavities (→ axial dispersion). If too high: insufficient eddy generation (→ bad mixing)

$$Str = \frac{d_e}{4\,\pi\,x_0}$$

- Oscillatory Reynolds number Re_o
  - >50 for flow separation (vortices)
  - >100 for “good” mixing
  - <250: 2D flow, axi-symmetric vortices, soft mixing regime
  - >250: 3D flow, no axial-symmetry, turbulent like

$$Re_o = \frac{2\,\pi\,f\,x_o\,\rho\,d_e}{\mu}$$

- Velocity ratio ψ: typically 2-10
  - ψ>1 for oscillatory flow to dominate the mixing regime

$$\psi = \frac{Re_o}{Re_n}$$

COBR operational windows

Summary of accepted ranges of Re_o, Str, Re_n, ψ for traditional OFRs*

Re_o	Str
50 (flow separation occurs)	<0.1 (fast stream core, strong shear)
>100 (minimal value for convection, i.e. sufficient mixing	>0.5 (effective eddy shedding)
<250 (flow 2-D, axi-symmetric, soft mixing regime)	**0.6 – 1.7 (minimum axial dispersion coeff.)**
>250 (flow 3-D, no axi-symmetry, turbulent-like)	

Re_n	ψ
>50 (minimal value for convection, i.e sufficient mixing)	>1 (maximum oscillatory velocity higher than net flow velocity
>80 (rapid mixing and uniformity)	**2-4 (optimal RTD conditions)**

*McGlone et al., *Org. Process Res. Dev.* 2015, 19, 1186−1202

Optional

Energy input

Mixing length for eddy enhancement model

$$\frac{P}{V} = \frac{1.5(2\pi f)^3 x_o^2 l_e}{L\alpha} \propto f^3 x_o^2 \qquad \left\{ \begin{array}{l} \text{low } x_o \ (1-5\ \text{mm}) \text{ and} \\ \text{high } f \ (3-14\ \text{Hz}) \end{array} \right.$$

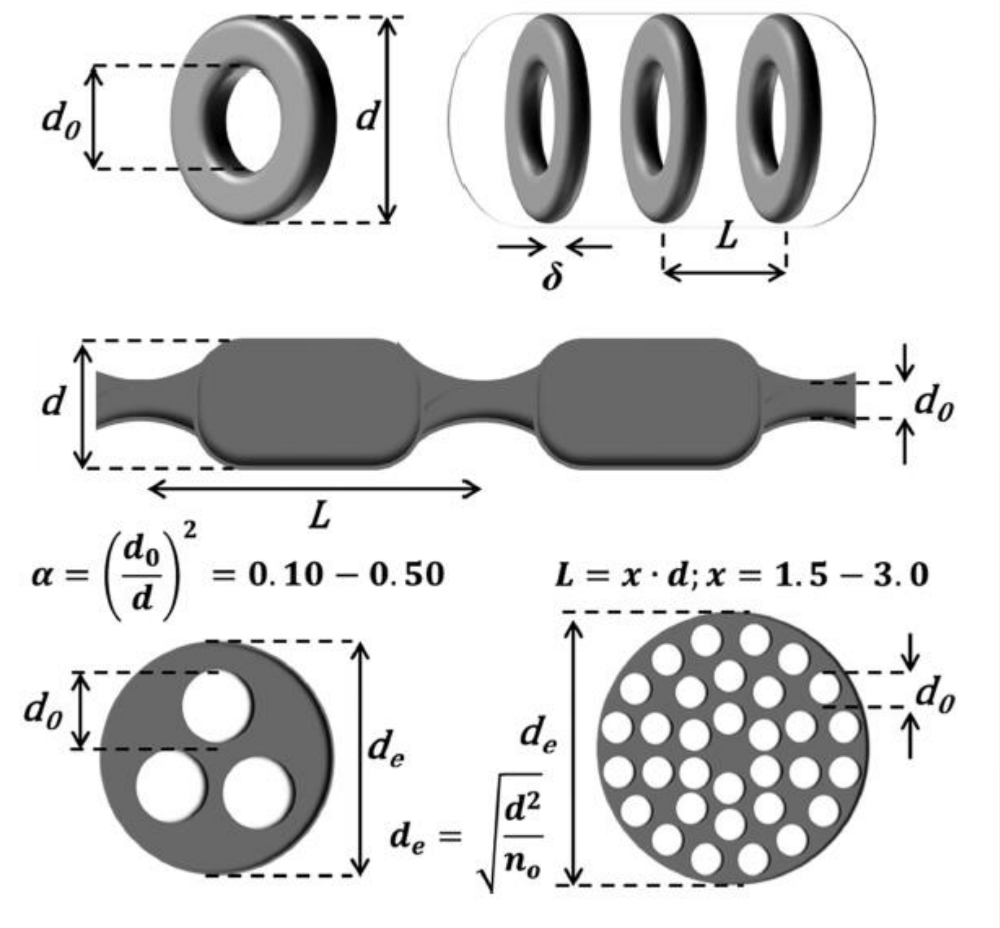
Number of baffles per unit length

$$\frac{P}{V} = \frac{2\rho N_b}{3\pi C_D^2}\left(\frac{1-\alpha^2}{\alpha^2}\right) x_o^3 (2\pi f)^3 \propto (f x_o)^3 \qquad \left\{ \begin{array}{l} \text{high } x_o \ (5-30\ \text{mm}) \text{ and} \\ \text{low } f \ (0.5-2\ \text{Hz}) \end{array} \right.$$

*Discharge coefficient of baffle**

*Related to baffle orifice size, usual value = 0.7

Baffle design



Single orifice baffle

Smooth periodic constriction

Multi-orifice baffle

McGlone et al., Org. Process Res. Dev. 2015, 19, 1186−1202

Heat transfer improvement

$$Nu = \frac{hd}{\lambda}$$

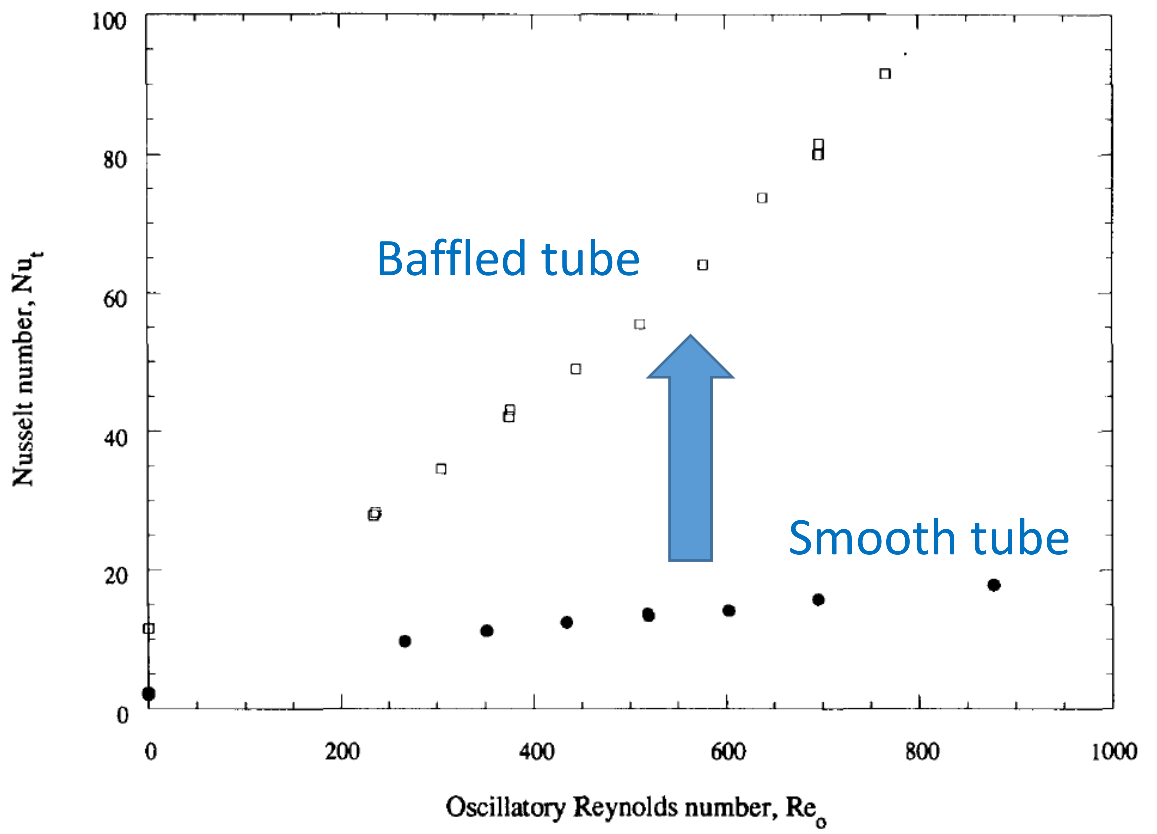
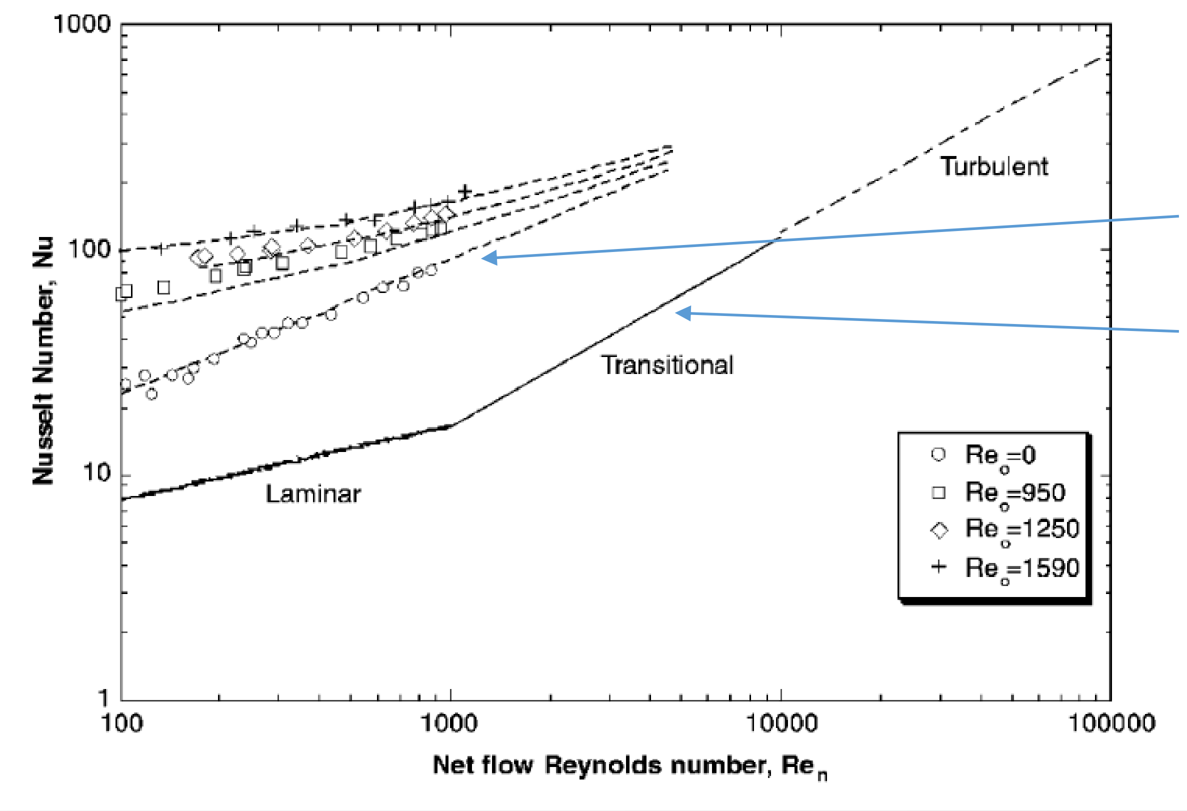


Fig. 3. Comparison of the heat transfer obtained in a smooth tube and a baffled tube where an oscillatory flow is superimposed on a low Re bulk flow: $Re_n = 130$, $Sr = 0.16$.

Mackley and Stonestreet, Chemical Engineering Science, Vol. 50, No. 14, pp. 2211 2224, 1995

Heat transfer improvement



Baffled tube, $Re_o=0$

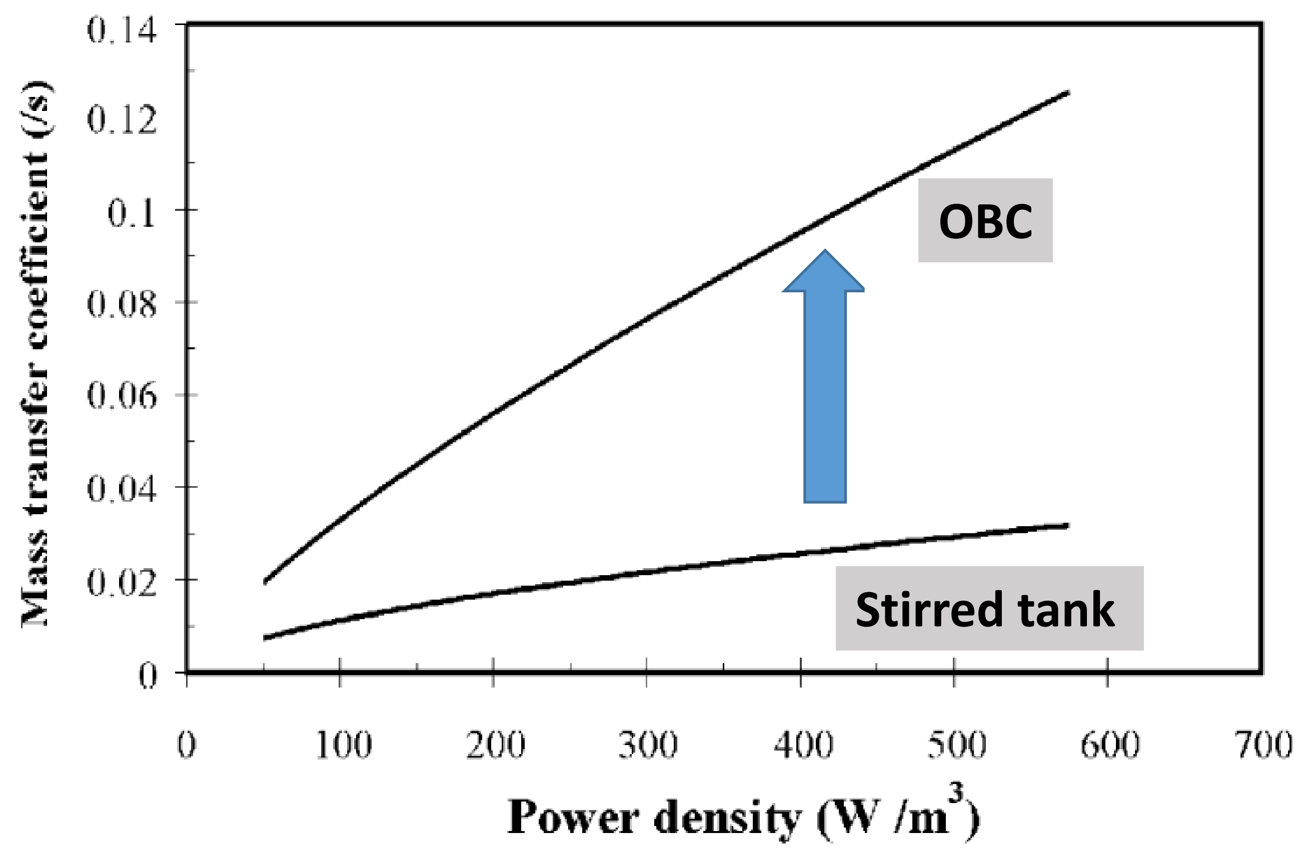
Smooth tube, $Re_o=0$

$$Nu = \frac{hd}{\lambda} = 0.0035\, Re_n^{1.3} Pr^{1/3} + 0.3\left[\frac{Re_o^{2.2}}{(Re_n + 800)^{1.25}}\right]$$

$$100 < Re_n < 1200$$
$$0 < Re_o < 800$$

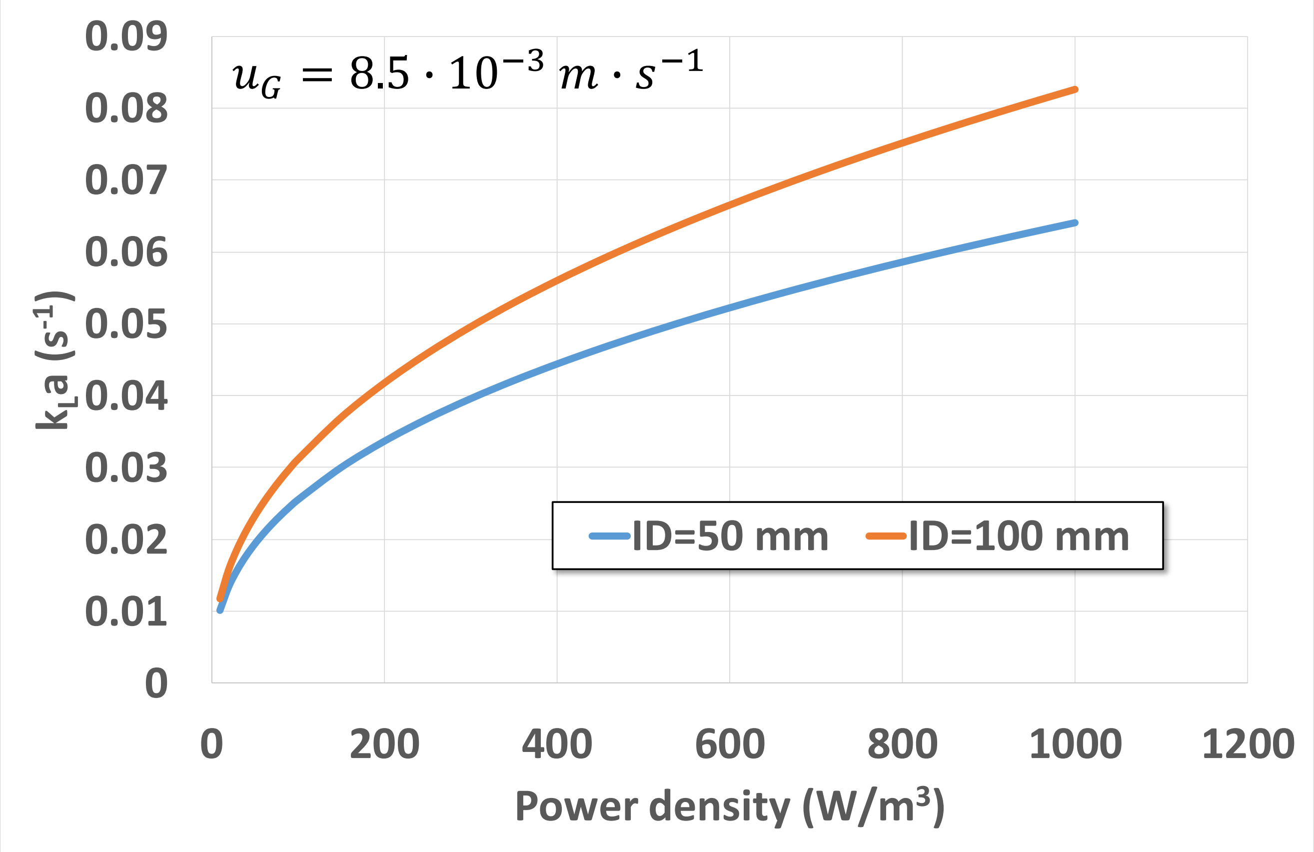
Mackley and Stonestreet, Chemical Engineering Science, Vol. 50, No. 14, pp. 2211 2224, 1995

Increase in mass transfer coefficient



Ni et al., Chem. Eng. Res. Des. 2003, 81, 373

Correlations for gas-liquid mass transfer coefficient



100 mm ID

$$k_La = 0.0256\left(\frac{P}{V}\right)^{0.425} u_G^{0.37}$$

$$4.24 \cdot 10^{-3} < u_G < 16.96 \cdot 10^{-3} m \cdot s^{-1}$$

50 mm ID

$$k_La = 0.0186\left(\frac{P}{V}\right)^{0.4} u_G^{0.32}$$

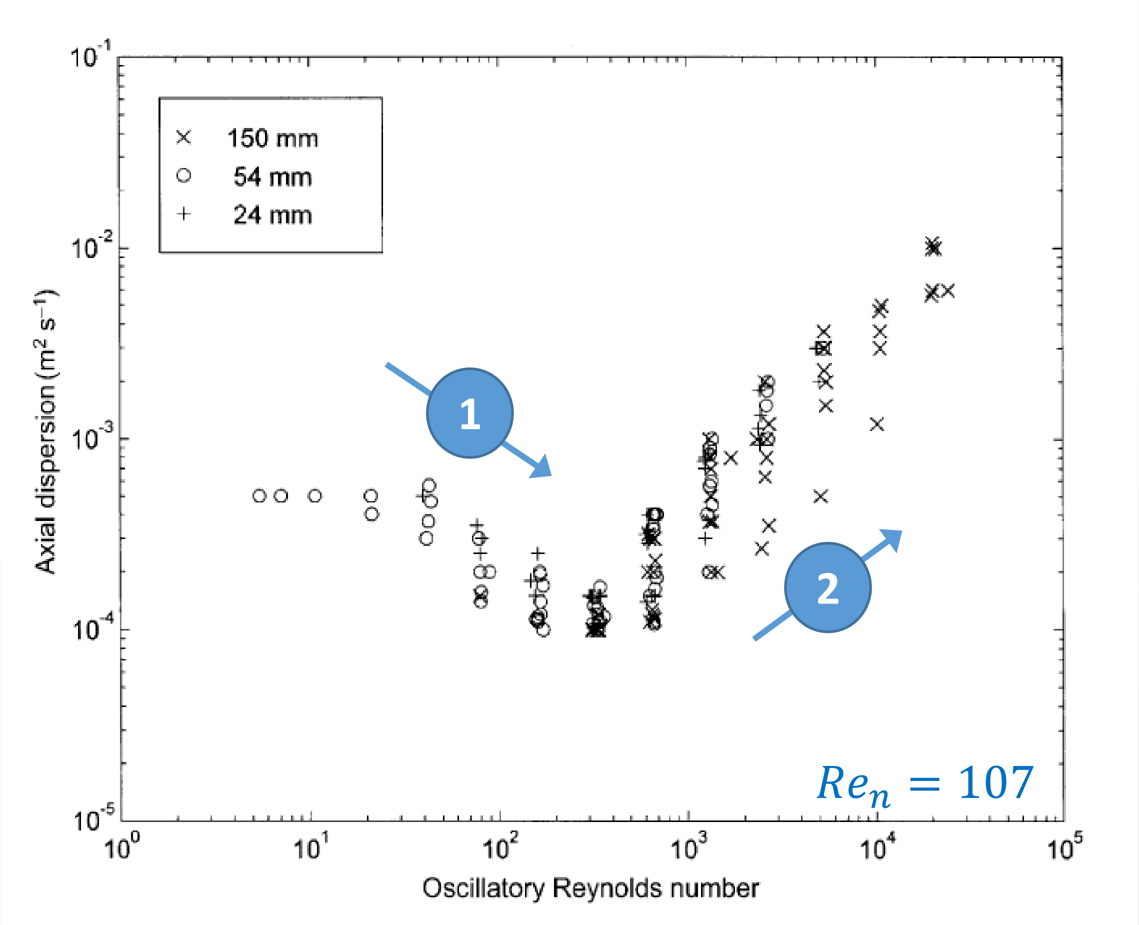
$$2.12 \cdot 10^{-3} < u_G < 8.48 \cdot 10^{-3} m \cdot s^{-1}$$

Mass transfer performance is better for larger reactor
→ Scale-up at constant P/V ensures at least equivalent k_La

X. Ni, S. Gao / The Chemical Engineering Journal 63 (1996) 157-166

RTD in COBRs

$$Re_o = \frac{2\,\pi\, f\, x_o\, \rho\, d_e}{\mu}$$

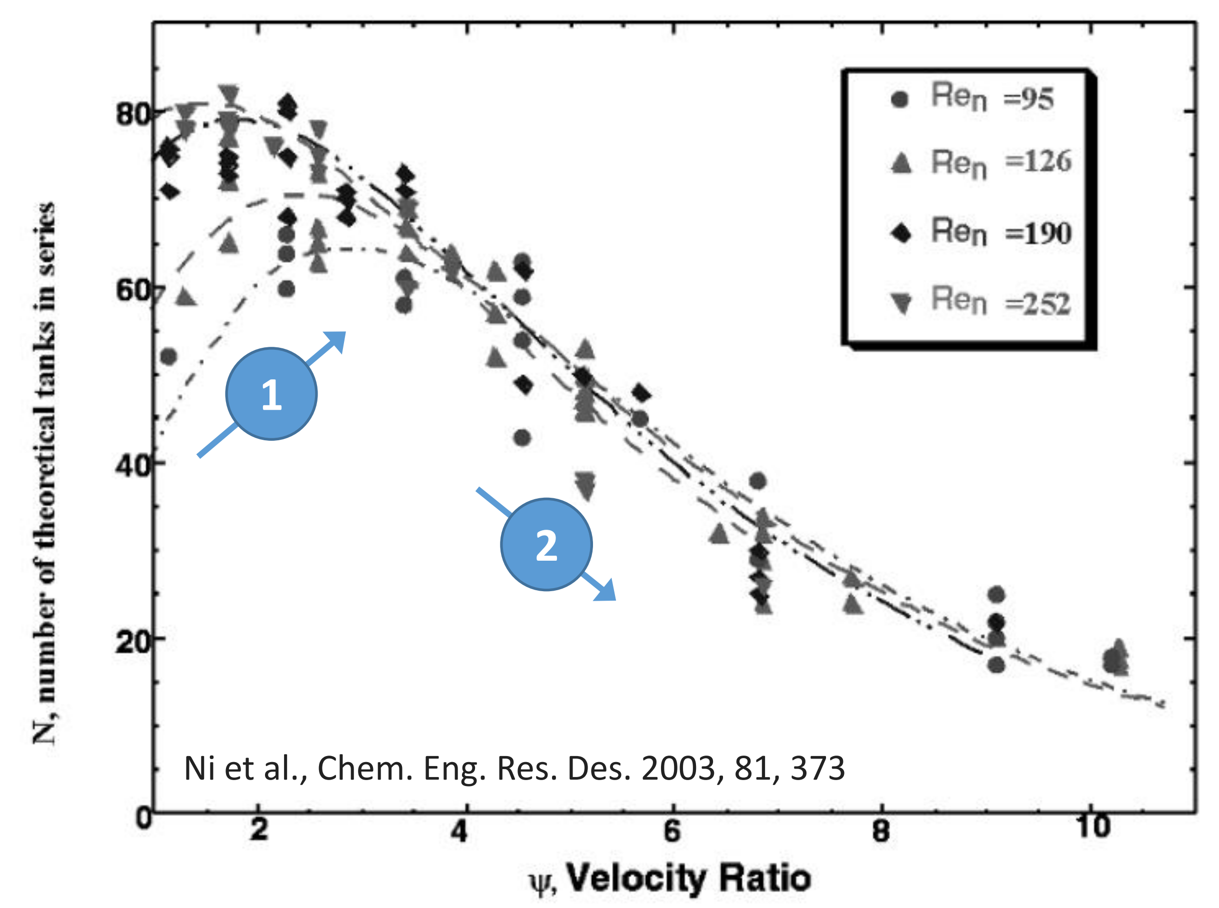


1. Increasing radial dispersion (vortices gradually fill chamber)
2. Increasing axial dispersion (vortices spread to adjacent chambers)

Smith and Mackley, Chemical Engineering Research and Design, 2006, 84(A11): 1001–1011

RTD in COBRs

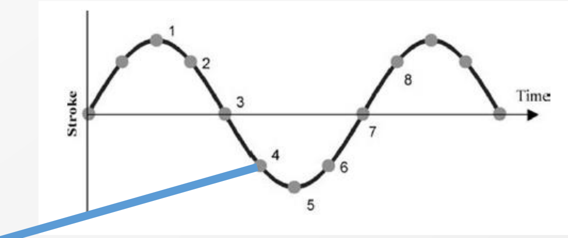
$$\psi = \frac{Re_o}{Re_n}$$

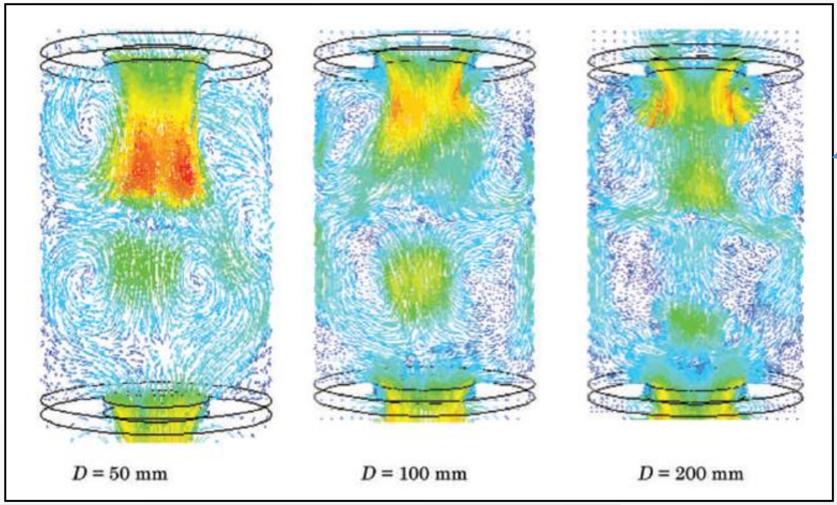


Ni et al., Chem. Eng. Res. Des. 2003, 81, 373

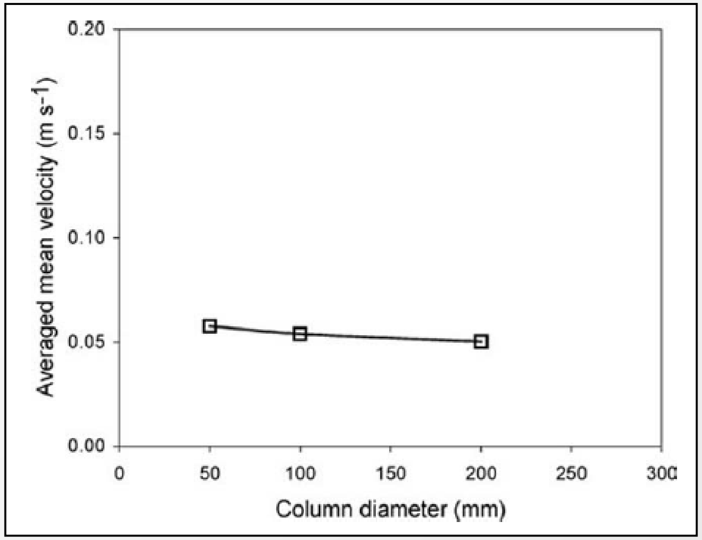
1. Increasing radial dispersion (vortices gradually fill chamber)
2. Increasing axial dispersion (vortices spread to adjacent chambers)

“Linear” scale-up





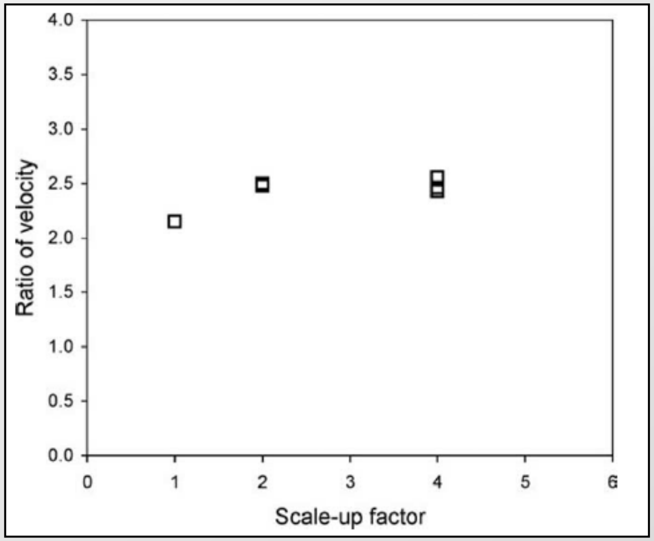
Velocity vector map: similar pattern at different diameters



$$\alpha = 0.22$$

$$\frac{L}{D} = 1.5$$

$$\psi = 2.5$$



Velocity and velocity ratio (axial/radial) independent of diameter → “linear” scale-up

Jian and Ni, Chemical Engineering Research and Design, 83(A10): 1163–1170

2.3 Continuous oscillatory baffled reactors

2.3.3 Crystallization in COBRs

Enhancement of crystallization processes

Use of Continuous oscillatory baffled crystallizers (COBC)

Advantages of COBCs

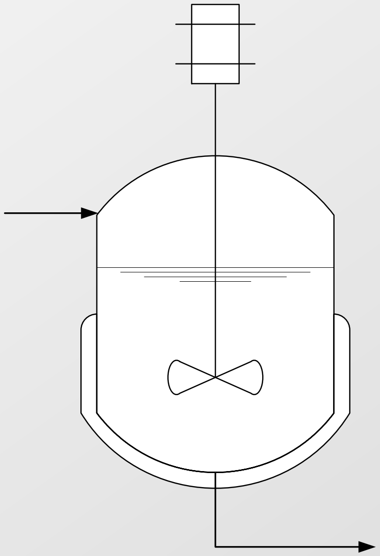
- Each particle experiences similar processing time (narrow RTD) and conditions (narrow shear rate distribution)→ narrow CSD with consistent purity/properties
- High mass transfer → narrow MSZW
- No impeller → no attrition and secondary nucleation

Disadvantages of COBCs

- Encrustation (fouling)
  - Mitigation e.g., by using ultrasound, seeding, T cycling, surface coating, …

MSMPR drawbacks

- MSMPR (mixed suspension mixed product removal)
  - High localized shear regions (impellers)
  - Non uniform temperature
  - Solids buildup in transfer lines
  - Non-linear scalability

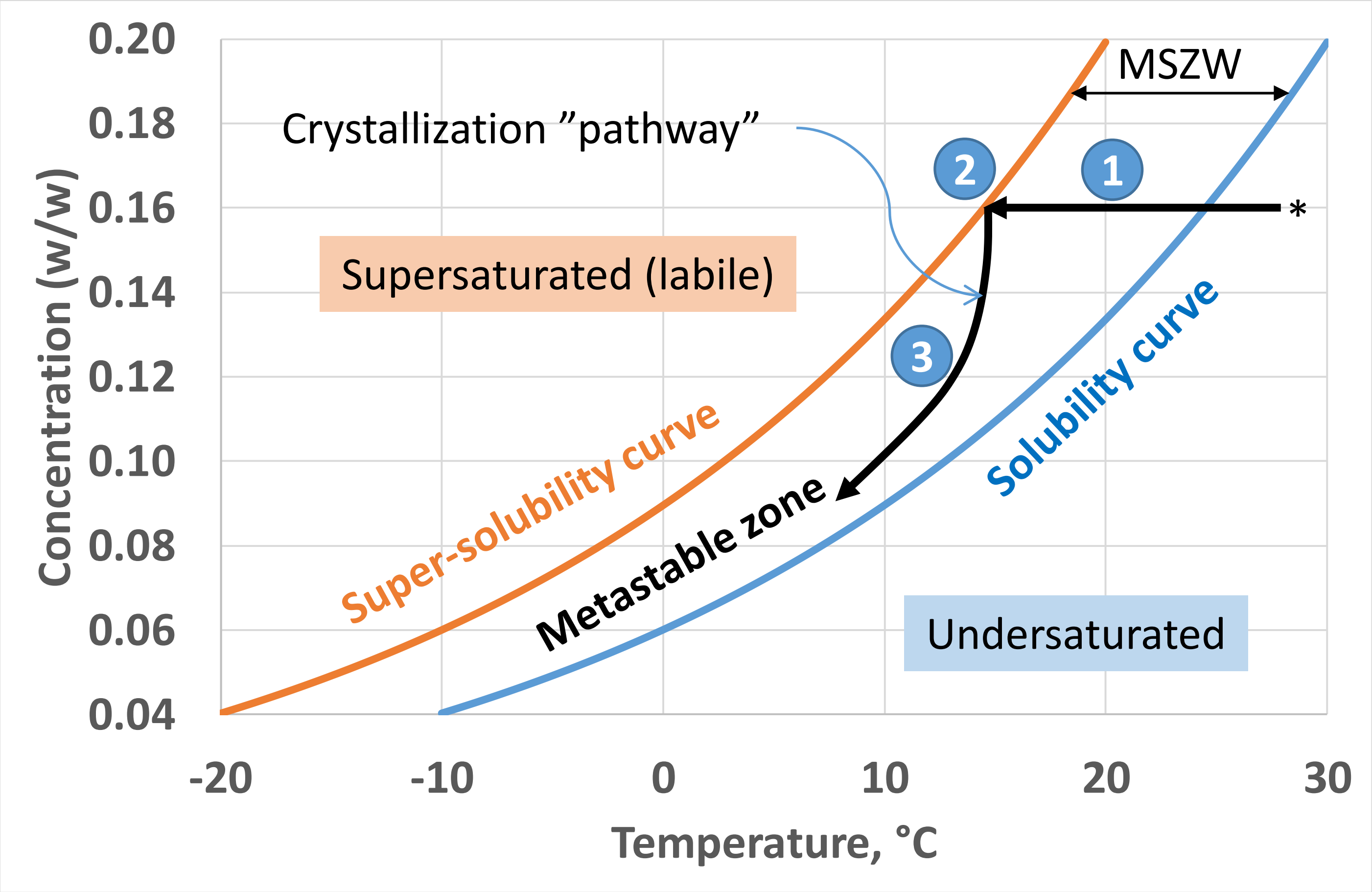


Enhancement of crystallization processes

Benefits of continuous oscillatory baffled crystallizers (COBC)

- Better control of
  - Crystal morphology (habit)
  - Crystal polymorphic form
  - Crystal purity
  - Crystal size
  - Crystal size distribution
  - Cake filterability
- Reduction of crystallization time
- Lower footprint
- Lower energy consumption

Essentials of crystallization



1. Cooling of starting solution
2. Nucleation
3. Growth

Supersaturation

- Supersaturation is the difference between system conditions and equilibrium.
- It is the driving force for nucleation and growth
- It can e.g., be described by the following relationships

$$S = \frac{c}{c^*}$$

Equilibrium concentration (solubility)

$$s = \frac{c - c^*}{c}$$

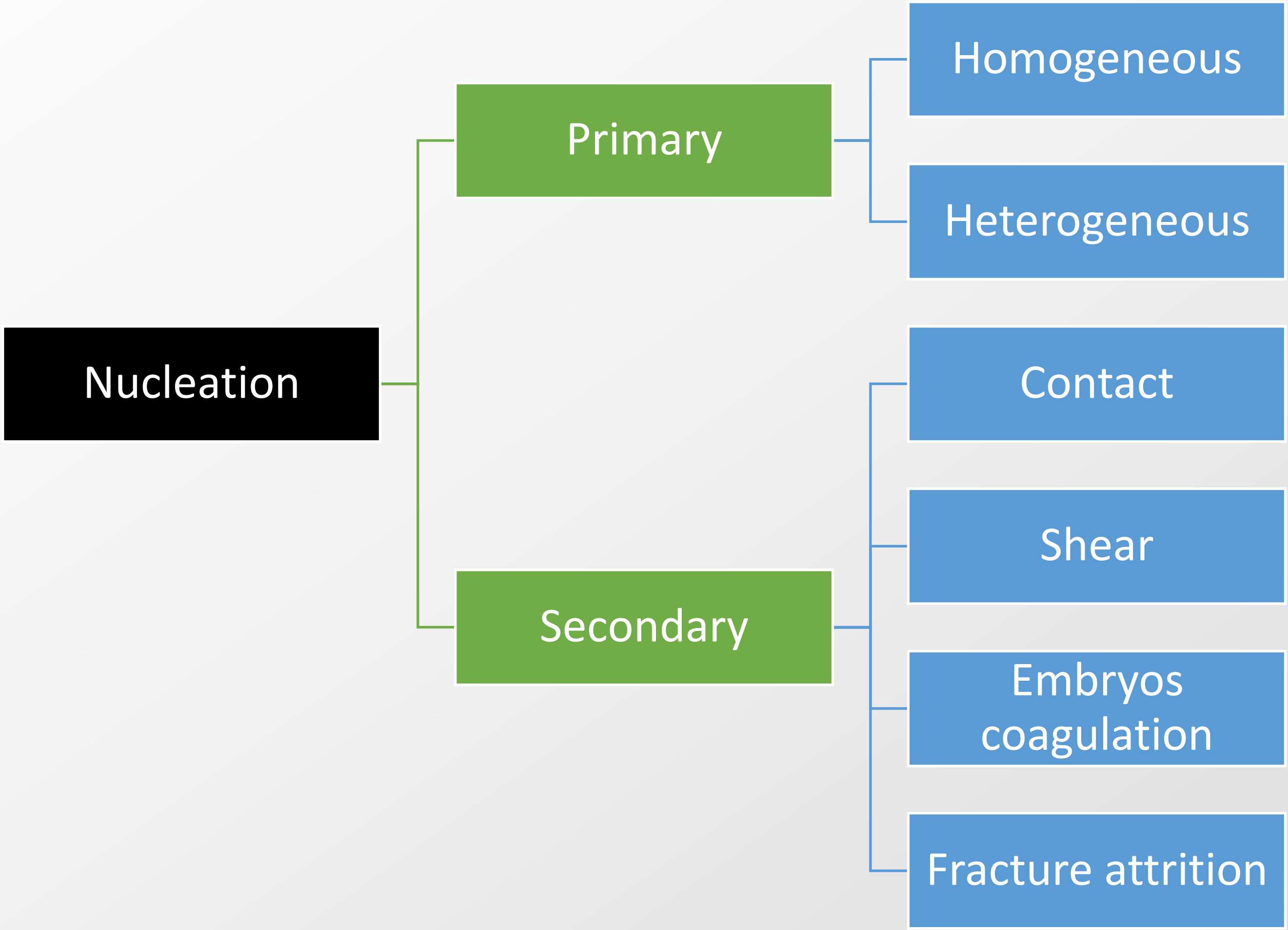
Solubility vs metastable limit

- The solubility curve can be determined experimentally as solubility is a thermodynamic property of the mixture
- However, the metastable limit is not well defined and depends on the process conditions. It is scale-dependent.
    - Cooling rate (rate of generation of supersaturation)
    - Reactor geometry
    - Agitation rate (fluid dynamics)
    - Impurities

Methods of generation of supersaturation

- Cooling
- Evaporation
- Evaporative cooling
- Chemical reaction
- Salting out
- Anti-solvent crystallization
- Direct-contact cooling
- pH adjustment

Nucleation mechanisms



Nucleation

Primary

Homogeneous

Heterogeneous

Secondary

Contact

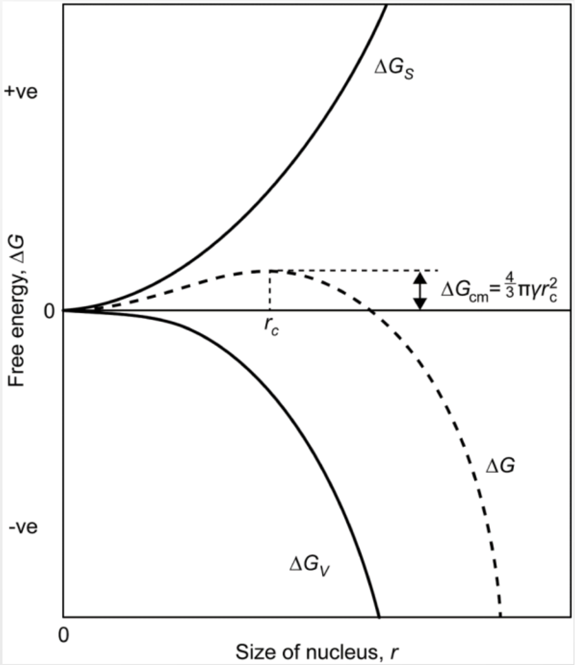
Shear

Embryos coagulation

Fracture attrition

Nucleation mechanisms

- **Primary** (product crystals not involved)
  - **Homogeneous** (spontaneous, no solid/liquid interface)
  - **Heterogeneous** (induced by other solids, foreign material such as dust)
  - ○ Occurs at high level of supersaturation
  - ○ High order dependence on supersaturation
  - ○ Occurs frequently in precipitations
  - ○ Happens in unseeded batch operation



Erdemir, D., Lee, A., & Myerson, A. (2019). Crystal Nucleation. In A. Myerson, D. Erdemir, & A. Lee (Eds.), Handbook of Industrial Crystallization (pp. 76-114). Cambridge: Cambridge University Press.

Nucleation mechanisms

- **Secondary** (induced by crystals)
  - Industrial crystallizers mostly operate in this nucleation regime (low supersaturation → secondary rather than primary nucleation)
  - Collisions crystal / crystal, crystal / internals, crystal / impeller or pump
  - Controlled by contact, shear, fracture, attrition, initial breeding (seeding)
  - Lower order dependence on supersaturation than homogeneous nucleation
  - Impacted by supersaturation, impact energy, viscosity, solvent, hardness of crystals/internals, impurities, size of crystals, impeller design/rpm

Primary nucleation rate
(homogeneous and heterogeneous)

$$\boxed{B^o = k_N s^n \propto s^n}$$

$$3 \leq n \leq 10$$

B^o	*Nuclei formed/unit volume/unit time*
k_N	Rate constant, function of T
s	*Supersaturation*
n	*Power function exponent*

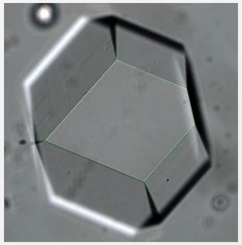
Secondary nucleation rate

$$\boxed{B^o = k_1 M_T^j s^b \propto s^b}$$

$$2 \leq b \leq 5 \quad 1 \leq j \leq 1.5$$

B^o	*Nuclei formed/unit volume/unit time*
k_1	Rate constant, function of T
s	*Supersaturation*
M_T	*Slurry density*
b and j	*Power function exponents*

Growth



- Molecular or bulk transport of the solute molecules from the surrounding solution to the crystal face
- Integration or incorporation of the solute molecules into the crystal surface (lattice)
- Characterized by following power law

$$\boxed{G = \frac{dl}{dt} = k_G s^g \propto s^g} \quad 1 \leq g \leq 2$$

l	*characteristic crystal length*
s	*supersaturation*
k_G	*function of T, rpm, impurities and system*
g	*system-specific*

Nucleation vs growth kinetics

Secondary nucleation: $B^o \propto s^b$

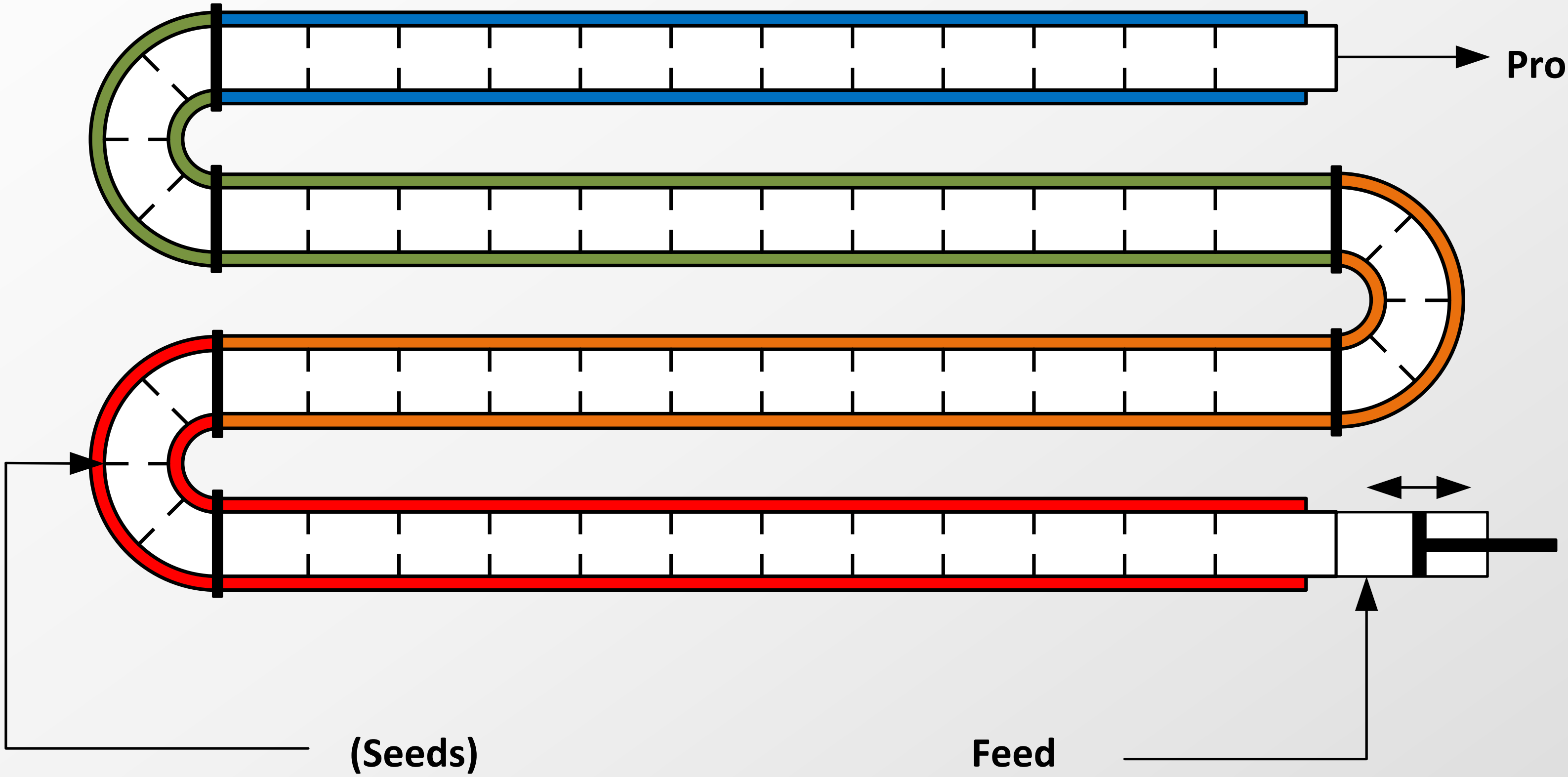
Growth: $G \propto s^g$

$$\boxed{\frac{G}{B^o} \propto s^{\overbrace{g-b}^{<0}}}$$

Usually: $g < b$

→ Operate crystallizer at <u>low supersaturation</u> in order to favor growth vs nucleation

Seeded cooling crystallization in COBC



Progressively decreasing temperature profile

Example COBR vs batch crystallizer

AstraZeneca: API isolation & purification by crystallization

- ✓Easier scale-up (flow conditions similar from lab to plant)
- ✓Crystallization time reduced from ~10 h → 12 min
- ✓Lower investment costs
- ✓Lower operational costs
- ✓Suppression of milling step

Lawton et al., Organic Process Research & Development, 2009, 13, 1357-1363