

FUNDAMENTAL STUDY OF SHEAR CONTROLLABLE SYNTHESIS OF FINE PARTICLES USING TAYLOR-COUETTE FLOW REACTOR

by

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DEDICATION

To my parents, for their unconditional love, support and encouragement, and for always being there for me. To my naughty but lovely little brother and sister, for their love, innocence, and hope for life.

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SYNOPSIS

Fine particles generally have special physicochemical properties, such as good solubility, dispersibility, and adsorption due to their extremely large specific surface area. With such advantages, they have been attracting wide attention in the fields of pharmaceuticals, catalyst, food, cosmetics, chemicals and electronics. Among various methods to prepare fine particle materials, reactive precipitation presents its advantages in terms of simple configuration, flexible operation, and low cost.

Controllable synthesis of fine particles is still a challenge. On one hand, fine particles have a tendency to aggregate or agglomerate due to the relatively reduced effect of gravity force and the enhanced effect of other surface forces, such as van de Waals force. On the other hand, operating conditions, especially the heterogeneity of fluid flow in chemical reactors have complex interaction with particles. Fluid mixing determines the environment for chemical reaction, and fluid shear, especially turbulence induced shear, affects particle growth. Since final material performance depends on particle properties, such as particle size, morphology, porosity, and tap density, it is necessary to investigate the key steps and processes on the course of particle formation in order to realize controllable synthesis and obtain desired products consequently. Thus, this PhD work aims to build the quantitative relationships between the key hydrodynamic parameters involved in the synthesis process using the Taylor-Couette flow (TC) reactor and the synthesised particle properties by employing such reactor. The main work conducted and outcomes derived from the project are summarised as follows:

(1) In chapter 2, barium sulfate was selected as a model substance to study the interfacial phenomenon during the process of particle formation. This chapter is mainly focused on the effect of hydrodynamic process in the TC reactor on particle morphology. Three different kinds of morphology of barium sulfate particles are observed by changing Reynolds number $Re = \frac{\omega dr_i}{\nu}$, feeding rate and supersaturation in the Taylor-Couette flow reactor with a lobed inner cylinder (LTC). Such morphology transition, indicating an interfacial interaction between feed solutions and aggregated particles, is found to be dependent on fluid flow pattern. The mechanism of particle formation under the effect of fluid dynamics is proposed for the LTC.

(2) Following the work of Chapter 2, Chapter 3 is focused on the change of barium sulfate particle size and particle size distribution. The comparison of the particles synthesised using the classical Taylor-Couette flow reactor (CTC) and the LTC reactor was conducted both experimentally and numerically by applying computational fluid dynamics (CFD) modelling. Particles synthesized in the LTC show the overall smaller size with narrower size distribution than those in the CTC, which is also consistent with the CFD modelling results on the effect of shear rate distribution on the particle size distribution. It is suggested that the local turbulence intensification due to geometry modification to the LTC inner cylinder is beneficial to the synthesis of particles with smaller size. Shear induced by small turbulent eddies can have a significant impact on the synthesised particle size.

(3) Chapters 2 and 3 have confirmed that hydrodynamics plays an important role in determining the synthesised particle properties. As the mixing occurring in the TC reactor creates supersaturation, which subsequently induces chemical reaction, a fundamental study on the mixing was carried out in Chapter 4. Based on the Villermaux iodide-iodate reaction system, the segregation index (Xs) was employed as an indicator to evaluate the micromixing efficiency. It is found that the hydrodynamic heterogeneity created by the LTC can significantly enhance the micromixing efficiency. Also, it has been reaffirmed that the micromixing time achieved in the TC reactor is about three orders of magnitude lower than that of the conventional stirred tank reactor. The alteration of the configuration of the inner cylinder can be seen as an effective method to intensify the process of particle preparation.

(4) As the features of Taylor vortices in the TC reactor have been used for particle preparation in this work, the interactions between the vortices embedded with turbulent eddies and the particles were investigated based on tracking the barium sulfate particle trajectories, as discussed in Chapter 5. The simulation reveals that particle motion exhibits a helical movement, entrapped by Taylor vortices. The effective particle diffusion coefficient was introduced in this chapter, which is enhanced by increasing the inner cylinder rotational speed, especially for the LTC, implying that the deformation of Taylor vortices in the gap region of the LTC may significantly affect the entrainment of the particles by such vortices and embedded turbulent eddies. Moreover, particle radial distribution may provide a guidance for particle classification due to the axial velocity gradient, while axial dispersion can be seen as an indicator to characterise the global mixing, which is found to distribute similar to the shape of particle size distribution, indicating the existence of a strong correlation between particle property and particle dispersion due to the turbulence eddies induced shear in the TC reactor. The results from particle tracking simulation are consistent with the previous studies on the hydrodynamics of the LTC that the use of LTC can intensify the process for particle preparation.

(5) The fundamental study of barium sulfate particle preparation in this PhD project indicates that turbulence eddy induced shear and micromixing occurring in the TC reactor will be beneficial to the realisation of controllable synthesis of fine particle materials. Thus, as an extension of the application, the LTC reactor was also employed for the other reactive system, the co-preparation of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ (NCM622) particles. Both CFD simulation and experimental results clearly show that the synthesized NCM622 particle properties have been improved in the LTC even with a reduced production time of 8 hours, compared to the conventional production method. Reactant mixing was assessed and characterized by two variables using CFD modelling with user-defined scalar (UDS). CFD modelling results show that the effective mixing at both the macro-scale and micro-scale can be quickly achieved in the LTC.

To sum up, this PhD work provides physical insight into the principle of controllable synthesis of fine particle materials. The implication is that the mixing in the TC reactor can create effective supersaturation, thereby inducing reactive precipitation under the effect of hydrodynamic heterogeneity. Such well-established mixing/micromixing environment can be quickly obtained in the TC reactors, especially in the LTC. Meanwhile, the shear induced by various length scale turbulent eddies embedded in the Taylor vortices has a strong correlation with the synthesized particle characteristics. Focuses should be placed on determination of appropriate operation parameters in the actual particle synthesis process when using the TC reactor.

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NOMENCLATURE

CHAPTER 1

А	embryos surface area, m ²
В	contact nucleation rate, m ⁻³ s ⁻¹
c	molar concentration, mol/L
ci	molar concentration at crystal-solution interface, mol/L
c*	molar concentration at equilibrium, mol/L
c _{ie}	species molar concentration in the local environment, mol/L
Cint	molar concentration at interface, mol/L
C _B	slab deformation rate constant
C _p	specific heat capacity, J/K/kg
d_{m}	molecular diameter, m
Di	molecular diffusion coefficient, m ² /s
D _R	stirred impeller diameter, m
E	engulfment rate, s ⁻¹
f	reactor friction factor
g	overall crystal growth rate, m/s
g(t)	volume growing rate in incorporation model
Gc	crystal growth rate, m/s
G	average shear rate, s ⁻¹
ΔG	total molar Gibbs free energy, J/mol
ΔG_{v}	free energy due to phase change, J/mol
ΔG^*	homogenous nucleation energy barrier, J/mol
ΔG^*_{het}	heterogeneous nucleation energy barrier, J/mol

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h	contact nucleation rate exponent
i	contact nucleation rate exponent
j	contact nucleation rate exponent
\mathbf{J}_{homo}	homogenous nucleation rate, m ⁻³ s ⁻¹
\mathbf{J}_{het}	heterogeneous nucleation rate, m ⁻³ s ⁻¹
k	contact nucleation rate exponent
k _B	Boltzmann's constant, J/K
k _D	mass transfer constant, m ⁴ /(kmol·s)
k _d	mass transfer coefficient, m/s
kg	total growth coefficient, m/s
k _G	overall growth rate constant, m/s
k _n	chemical reaction rate constant
k _R	surface integration constant, $m(dm)^6/(mol^2 \cdot s)$
k _T	thermal conductivity, W/m/K
Κ	induction time constant
$K_{\rm N}$	nucleation rate constant
\mathbf{l}_{eddy}	Kolmogorov length scale, m
l _{meso}	meso-mixing length scale, m
L	crystal size, m
L _R	length of reactor, m
М	molecular molar mass, g/mol
M_{T}	particle mass density, g/m ³
n	kinetic order of nucleation
n	unit normal vector
n _{A0}	initial mole of reactant A
n _{B0}	initial mole of product B
n _{C0}	initial mole of reactant A

n _R	net mole of product R
ns	net mole of by-product S
n*	number of molecules forming the critical embryo nuclei
N	stirred frequency, s ⁻¹
р	static pressure, Pa
Q	volumetric bulk flow rate, mL/s
Qfeed	volumetric flow rate of feeding steam, mL/s
r	nucleus radius, m
r _c	critical nucleus radius, m
r _i	radius of the inner cylinder, m
r _o	radius of the outer cylinder, m
Re	Reynolds number
R_i	chemical reaction rate, mol/m ³ /s
S	supersaturation ratio/ source term
Sc	Schmidt number
Т	thermodynamic temperature, K
Та	Taylor number
u	fluid velocity in x direction, m/s
u	fluid velocity vector, m/s
ū	fluid local mean velocity, m/s
V	fluid velocity in y direction, m/s
Ve	embryo volume, m ³
Vie	fluid element volume in incorporation model, m ³
V _R	reactor volume, m ³
W	fluid velocity in z direction, m/s
Xs	segregation index
Y	yield of by-product S

β	aspect ratio
3	turbulent energy dissipation rate, m ² /s ³
η	radius ratio
μ	molecular dynamic viscosity, kg/(m·s)
ν	kinematic viscosity of the fluid, m^2/s
ρ	density of the fluid, kg/m ³
ρ_c	crystal density, kg/m ³
σ	surface free energy per unit area, J/mol/m ²
τ	shear stress strain rate, $kg/(m \cdot s^2)$
$ au_{m}$	characteristic mixing time, s
$ au_{macro}$	macromixing time, s
$ au_{meso}$	meso-mixing time, s
$ au_{micro}$	micromixing time, s
τ_{N}	nucleation induction time, s
τ_{R}	characteristic chemical reaction time, s
ω	rotational speed, rad/s
λ	reactor length scale factor, m
Ω	pre-exponential factor for homogenous nucleation
Ω_{het}	pre-exponential factor for heterogeneous nucleation
Φ	generalized variable
$\Phi_{\rm s}$	slab deformation rate, s ⁻¹
Γ	generalized diffusion coefficient, m/s

а	ion activity, mol/kg
Ai	cross sectional area of the inner cylinder, m
В	growth rate, m/s
с	molar concentration, mol/L
Δc	concentration difference, mol/L
d	diameter of particle, m
D	molecular diffusion coefficient, m^2/s
E	engulfment rate, s ⁻¹
f	friction factor
G	shear rate, s ⁻¹
Ι	ionic strength, mol/kg
J	nucleation rate, m/s
k _{aggl}	agglomeration rate
Kg	total growth coefficient, m/s
K _{sp}	thermodynamic solubility product, mol^2/L^2
1	length scale, m
l _m	size of agglomerating particle m, m
ln	size of agglomerating particle n, m
L	reactor length, m
n	kinetic order of nucleation
Pe	Peclet number
Q	feeding rate, mL/min
r i	equivalent radius of the lobed inner cylinder, m
r _o	radius of the lobed outer cylinder, m
R	gas constant, J/(mol·K)
Re	Reynolds number
R _i	perimeter of the inner cylinder, m

S	saturation ratio
Sa	supersaturation ratio
Sc	Schmidt number
Sh	Sherwood number
St	Stokes number
t _D	diffusion time, s
t _N	induction time, s
t _m	micro-mixing time, s
Т	absolute temperature, K
ut	terminal velocity of particle, m/s
u_{θ}	azimuthal velocity, m/s
V	volume of reactor, m ³
Z	charge number

β_{aggl}	agglomeration efficiency
γ_{\pm}	activity coefficient
δ_{eq}	equivalent gap, m
Γ	aspect ratio
3	turbulent energy dissipation rate, m^2/s^2
ζ	angular velocity ratio
η	radius ratio
$\dot{\eta}_V$	volume shear rate, mL/s
λ_{eddy}	eddy length scale, m
μ	viscosity of the fluid, $kg/(m \cdot s)$
ρ_d	density of particle, kg/m ³
σ	supersaturation

υ	kinematic viscosity of the fluid, m ² /s
φ	molar chemical potential, J/mol
ω _i	rotational speed of the lobed inner cylinder, rad/s

a _i	ion activity of species i, mol/kg
a _{eq}	ion activity at equilibrium state, mol/kg
Ai	cross sectional area of the inner cylinder, m
В	growth rate, m/s
$C_{1\epsilon}$	model constant for ε equation
$C_{2\epsilon}$	model constant for ε equation
C_{μ}	model constant for the calculation of μ_t
d _p	particle size, m
d	gap width, m
D	average crystallite sizes, nm
g	gravity, m/s ²
G	local shear rate, s ⁻¹
G _k	generation of turbulence kinetic energy, J
J	nucleation rate, m/s
k	turbulent kinetic energy, m^2/s^2
kg	growth coefficient, m/s
k _N	nucleation coefficient, m/s
K	shape factor
K _{SP}	thermodynamic solubility product, mol^2/L^2
l _{eddy}	Kolmogorov length scale, m
L	reactor length, m
n	kinetic order of nucleation rate

р	pressure, Pa
Q	volumetric feeding rate, mL/min
r _i	radius of the inner cylinder, m
ro	radius of the lobed outer cylinder, m
R	correlation coefficient
Re	Reynolds number
R_i	perimeter of the inner cylinder, m
R_{ϵ}	extra strain rate, s ⁻¹
S	supersaturation ratio
St	Stokes number
t _m	micromixing time, s
t _{res}	average residence time, s
u	fluid velocity, m/s
ut	terminal velocity, m/s
V	volume of the reactor, mL

β	model constant for the correction of $C_{1\epsilon}$ term in the ϵ equation
γ	shear strain rate, s ⁻¹
3	turbulent energy dissipation rate, m ² /s ³
η	model constant for the correction of $C_{1\epsilon}$ term in the ϵ equation
η_0	model constant for the correction of $C_{1\epsilon}$ term in the ϵ equation
μ	dynamic viscosity, kg/(m·s)
μ_{eff}	effective viscosity, kg/(m·s)
μ_{t}	turbulent viscosity, $kg/(m \cdot s)$
ν	kinematic viscosity of the fluid, m^2/s
ρ	density of the fluid, kg/m ³

ρ_p	particle density, kg/m ³
σ_k	turbulent Prandtl number for k equation
σ_{ϵ}	turbulent Prandtl number for ε equation
τ	stress tensor, $kg/(m \cdot s^2)$
ω _i	rotational speed of the inner cylinder, rad/s
δ	peak width, nm
λ	wavelength of X-ray, nm
θ	diffraction angle, rad

A ₃₅₃	absorption at 353 nm
cj	concentration of species j, mol/L
d	gap width, m
Da	Damköhler number
e ₃₅₃	molar extinction coefficient, L/mol/mm
g	growing rate for incorporation model
Ι	turbulent intensity, %
\mathbf{I}_{i}	ionic strength, mol/L
k	reaction rate constant, m^2/s^2 , dimension dependent on reaction order
K ₃	equilibrium constant for Reaction (3)
L	reactor length, m
nj	mole of species j, mol
r	chemical reaction rate, mol/L/s
ľi	radius of the inner cylinder, m
r _o	radius of the lobed outer cylinder, m
Re	Reynolds number
R _{IXs}	correlation

t _m	micromixing time, s
tr	chemical reaction time, s
Т	thermodynamic temperature, K
Xs	segregation index
Y	yield of iodine

ν	kinematic viscosity of the fluid, m^2/s
ωi	rotational speed of the inner cylinder, rad/s
Ψ	thickness of quartz cell, mm

CD	drag coefficient
d_p	particle size, m
\bar{d}_p	size constant
d	gap width, m
d_{ij}	deformation tensor
Dz	diffusion coefficient, m ² /s
\mathbf{F}_{P-L}	external force, $kg/(m^2 \cdot s^2)$
g	gravity, m/s ²
k	turbulent kinetic energy, m^2/s^2
L	reactor length, m
\dot{m}_p	mass flow rate of particles, kg/s
\dot{M}_{L-P}	mass transfer rate, $kg/(m^3 \cdot s)$
n	size spread parameter
Ν	total number of particles
р	pressure, Pa

radius of the inner cylinder, m
radius of the lobed outer cylinder, m
Reynolds number
particle Reynolds number
Stokes number
instantaneous velocity, m/s
Reynolds-average velocity, m/s
velocity fluctuation, m/s
particle velocity, m/s
accumulated mass fraction of particle
axial position of the i th particle

3	turbulent energy dissipation rate, m ² /s ³
ν	kinematic viscosity of the fluid, m ² /s
ρ_L	liquid density, kg/m ³
$ ho_p$	particle density, kg/m ³
$\tau_{\rm L}$	stress tensor, $kg/(m \cdot s^2)$
τ_p	particle relaxation time, s
$ au_{\mathrm{f}}$	characteristic time of flow, s
ω _i	angular velocity, rad/s
Ω	rotational speed of the inner cylinder, rpm
μ	molecular viscosity, kg/(m·s)

CHAPTER 6

CA	concentration of reactant A, mol/L
CA0	initial concentration of reactant A, mol/L

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CB	concentration of reactant B, mol/L				
CB0	initial concentration of reactant B, mol/L				
$C_{1\epsilon}$	model constant for ε equation				
$C_{2\epsilon}$	model constant for ε equation				
C_{μ}	model constant for the calculation of μ_t				
C_{Φ}	mechanical-to-timescale ratio				
d_p	particle size, m				
d	gap width, m				
D	average crystallite sizes, nm				
g	gravity, m/s ²				
Ē	local shear rate, s ⁻¹				
G_k	generation of turbulence kinetic energy, J				
k	turbulent kinetic energy, m^2/s^2				
Κ	shape factor				
L	reactor length, m				
р	pressure, Pa				
r _i	radius of the inner cylinder, m				
ro	radius of the lobed outer cylinder, m				
R	correlation coefficient				
Re	Reynolds number				
R_{ϵ}	extra strain rate, s ⁻¹				
Sc_t	turbulent Schmidt number				
St_{η}	Stokes number				
t_{Φ}	micromixing time, s				
u	Reynolds-average velocity, m/s				
γ	micromixing rate, s ⁻¹				
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3	turbulent energy dissipation rate, m ² /s ³				
μ_{eff}	effective viscosity, kg/(m·s)				
ν	kinematic viscosity of the fluid, m^2/s				
ρ	density of the fluid, kg/m ³				
ρ_p	particle density, kg/m ³				
σ_k	turbulent Prandtl number for k equation				
σ_{ϵ}	turbulent Prandtl number for ε equation				
τ	stress tensor, $kg/(m \cdot s^2)$				
$ au_p$	particle relaxation time, s				
$ au_{\mathrm{f}}$	characteristic time of fluid flow, s				
$\bar{\xi}$	mean mixture fraction				
$\overline{\xi'^2}$	mean mixture fraction variance				
ω _i	rotational speed of the inner cylinder, rad/s				
δ	peak width, nm				
λ	wavelength of X-ray, nm				
θ	diffraction angle, rad				
$\Gamma_{\rm T}$	turbulent diffusivity, m/s				
η	Kolmogorov length scale, m				

CHAPTER 1

A LITERATURE REVIEW ON PARTICLE PRECIPITATION IN CHEMICAL REACTORS

SUMMARY

Reactive precipitation is commonly defined as the crystallisation of sparingly soluble substances formed by chemical reactions under high levels of supersaturation. It is an important and economical operation in the chemical industry due to its simplicity, the possibility of mass production, as well as low cost. Over recent decades, there has been a growing demand for particle materials with desired size, morphology, porosity, and tap density. In particular, fine particles (~1 μ m) have been found to have a wide range of applications to catalysts, pigments, pharmaceuticals, food, and cosmetics due to their superior properties. Reactive precipitation is suggested to be one promising method to prepare fine particle materials. For large scale production, this process generally take place in chemical reactors, while different reactors have different hydrodynamic features. Precipitation is induced by supersaturation, while supersaturation is generated by mixing, but reduced by nucleation and crystal growth. Furthermore, the formed particles are strongly influenced by hydrodynamic conditions, especially shear force. Therefore, reactive precipitation shows high complexity, involving many steps, such as nucleation, crystal growth, agglomeration, breakup, and Ostwald ripening. Also, the interaction between particles with flow field should be taken into account.

Considerable research works have been dedicated to the synthesis of fine particles with desired properties. However, controllable synthesis is still a big challenge. In this chapter, an elaborate literature review on particle precipitation in chemical reactors is presented, involving fundamentals of crystallisation and hydrodynamics, applications of chemical reactors, as well as an introduction to a particular case, Taylor-Couette flow reactor.

1.1 Reactive precipitation process

Reactive precipitation involves two basic procedures, i.e., chemical reaction and crystallisation (Nielsen, 1964; Mersmann, 2001; and Myerson 2002). Chemical reaction is triggered by the contact of reactants, while the extent of contact, including rate, interfacial area, and homogeneity is influenced by mixing. Once the mixed reactants achieve supersaturation, crystallisation can be induced. This consists of two major steps, nucleation and crystal growth, along with agglomeration and breakup. Figure 1.1 displays the relationship between these factors and the mechanism of reactive precipitation.



Figure 1.1 Mechanism of reactive precipitation and its influencing parameters, reproduced with permission (Schwarzer and Peukert, 2002, p.657).

1.1.1 Nucleation kinetics

During precipitation, new particles are generated by the nucleation process. Nuclei are originated from molecules, atoms or ions brought by the reactants in a supersaturated solution. The nucleation rate is defined as the number of nuclei formed per unit time, which plays an important role in determining particle properties, such as particle size and its distribution, particle morphology and growth orientation.

Based on the classical nucleation theory, there are two main basic nucleation modes: primary nucleation and secondary nucleation. The primary nucleation can be further categorised into homogenous nucleation and heterogeneous nucleation respectively (Becker, R. and Doring, 1935; Dirksen and Ring, 1991; and Nielsen, 1964).

1.1.1.1 Primary homogenous nucleation

Primary homogenous nucleation occurs in the absence of crystal interface. It assumes that solute molecules or ions combine together to produce embryos firstly in a supersaturated solution. The overall energy required for the formation of an embryo comes from two parts: one is used to create a new surface, and the other one is consumed to form a new volume (i.e., crystalline body). Therefore, the total free energy ΔG is expressed as (Muline, 2012),

$$\Delta G = V_e \Delta G_V + A\sigma \tag{1.1}$$

where V_e and A are the volume and surface area of the embryo respectively. ΔG_V is the free energy change associated with phase change, which is a negative value. σ is the surface free energy per unit area. For a spherical nucleus with a radius of r, the above Equation (1.1) can be converted into

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \sigma \tag{1.2}$$

The first term on the right-hand side of Equation (1.2) indicates a negative volume contribution, which is proportional to r^3 , while the second term represents the positive surface contribution, which is proportional to r^2 . Therefore, the overall dependence of the free energy ΔG on the radius of a nucleus r is illustrated in Figure 1.2. It is clear that ΔG reaches its maximum value at the critical nucleus size r_c . Those embryos, whose size are smaller than the critical nucleus size, are unstable and tend to dissolve and disappear due to the increase of free energy caused by embryo growth. On the contrary, any embryo with size larger than the critical nucleus size, is stale and tend to continuously grow into nucleus. The critical nucleus size r_c can be obtained by setting $\frac{d\Delta G}{dr} = 0$, expressed as

$$r_c = -\frac{2\sigma}{\Delta G_V} \tag{1.3}$$

Accordingly, substituting Equation (1.3) into Equation (1.2), the critical value of energy is obtained, which is referred to energy barrier for nucleation, expressed as

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_V^2} \tag{1.4}$$



Figure 1.2 Change of free energy with the radius of nucleus during nucleation process, highlighting the critical nucleus size, reproduced with permission (Muline, 2012, p.593).

Based on the pioneering study of Nielsen (1964), who adopted the terminology that nucleus denotes supercritical in size (i.e., $r > r_c$), while embryo is subcritical in size (i.e., $r < r_c$).

The rate of nucleation is derived by Nielsen (1964),

$$J_{homo} = \Omega exp(\frac{-16\pi\sigma^{3}V_{e}^{2}}{3k_{B}^{3}T^{3}(\ln S)^{2}})$$
(1.5)

where Ω is the pre-exponential factor, k_B is Boltzmann's constant, T is the thermodynamic temperature, and S is the supersaturation ratio. Also, S is known as the driving force for precipitation. Equation (1.5) indicates a powerful effect of supersaturation on homogenous nucleation due to the explosive increase in nucleation rate beyond the critical value of supersaturation. Also, nucleation can

potentially take place at any level of supersaturation. According to previous studies of Nielsen (1964), Nyvlt (1971), and Sohnel and Garside (1992), they proposed a simplified empirical form of nucleation rate for the application in crystallisation industry, expressed by

$$J_{homo} = K_N S^n \tag{1.6}$$

where K_N is the nucleation rate constant, and *n* is the kinetic order of nucleation, varying between 1 to 10 based on the physical properties and hydrodynamics of the reactive system (Baldyga, 2016).

1.1.1.2 Primary heterogeneous nucleation

Primary heterogeneous nucleation occurs in the presence of crystal interface from foreign substances, which may act as catalysts for nucleation process. Due to the smaller surface free energy of nucleus generating on the surface of the foreign seeds, the energy barrier and the critical supersaturation are lower than those of homogeneous nucleation, shown in Figure 1.3. Another difference is that once the heteronuclei are consumed completely, heterogeneous nucleation will be stop. The rate of heterogeneous nucleation has the same form as homogeneous nucleation, expressed as

$$J_{het} = \Omega_{het} exp(\frac{-\Delta G_{het}^*}{k_B T})$$
(1.7)



Figure 1.3 Effect of the supersaturation on different types of primary nucleation, reproduced with permission (Muline, 2012, p.593).

During the reactive precipitation, primary homogeneous nucleation is the rate determining step at a high supersaturation, while with the consumption of reactant, supersaturation is reduced, thus heterogeneous nucleation begin to dominate. These two types of nucleation take place in series. The total nucleation rate can be simply expressed as the sum of two rates, $J=J_{homo}+J_{het}$.

Heterogeneous nucleation is more likely to be induced in industry due to the exposure of other surfaces, such as impurities and rough surface of equipment.

1.1.1.3 Secondary nucleation

Secondary nucleation only takes place with the presence of existing crystals. Its mechanism is suggested to be classified into two categories: true secondary nucleation and contact secondary nucleation (Botsaris, 1976). In true secondary nucleation, nuclei are created when the supersaturation is higher than the

existing particles in solution. This is frequently observed in the ripening process. In contrast, secondary nucleation nuclei are formed due to crystal-crystal collision or crystal-wall collision. Garside and Davey (1980) proposed an empirical relationship of the contact nucleation rate from their experimental observation,

$$B = \lambda^h S^i M_T^j \omega^k \tag{1.8}$$

where λ is the length scale factor, M_T is the particle mass density, and ω depends on the agitating intensity of a given system, such as the stirring speed of a blade. The exponents *h*, *i*, *j*, and *k* are fixed values, which depend on the operating conditions.

This equation indicates that hydrodynamic shear force in terms of rotational speed has a significant influence on the contact secondary nucleation rate. When the supersaturated solution passes through the surface of a growing crystal, shear force has potential to sweep some attached nuclei from the crystal surface, forming new nuclei at other places (Powers, 1963; Sung *et al.*, 1973; Jagannathan *et al.*, 1980; and Wang *et al.*, 1981).

Generally, the nucleation rate is significantly dependent on supersaturation due to its high order of magnitude. A very small change of supersaturation will lead to a great fluctuation of nucleation rate. This may be a challenge for industrial production to obtain the desired products.

1.1.2 Growth kinetics

Once nuclei stably exist in a supersaturation solution, they will gradually grow into crystals. This mechanism can be described at two size scales: macroscopic and molecular (Mullin, 2000). Firstly, mass transport by either diffusion or convection is controlled by the concentration gradient, which will facilitate the mass motion from bulk solution to nuclei surface. Secondly, these newly attached mass is integrated into crystal lattice by surface reaction. Therefore, the interface between crystal and solution plays an important role in attaching mass. Two types of surface are involved: smooth and rough, shown in Figure 1.4. On a smooth surface, atoms from reactant molecules or ions are arrayed as an identical cube, where inside a crystal, any atom has six neighbours. This means that each atomic bond will share two atoms, leading to an increase of binding energy three times higher (Dirksen and Ring, 1991). However, for a rough surface, such binding energy will be reduced, and the growth rate of crystals on a rough surface will be larger than that on a smooth surface.



Figure 1.4 Two types of interface in a growing crystal: (a) smooth surface; and (b) rough surface, reproduced with permission (Dirksen and Ring, 1991, p.2396).

The growth rate of a crystal can be expressed by the linear growth of crystal surface, as follows,

$$G_c = \frac{dL}{dt} \tag{1.9}$$

where *L* is the crystal size.

Since the crystal growth can be either diffusion controlled or surface integration controlled, the both are driven by concentration gradient, shown in Figure 1.5. Therefore, Equation (1.9) can be converted into the following form,

$$G_c = k_D(c - c_i)$$
 diffusion controlled (1.10)

$$G_c = k_R (c_i - c^*)^r$$
 surface integration controlled (1.11)

where the mass transfer constant, $k_D = k_d M / \rho_c \cdot k_d$ is the mass transfer coefficient, *M* and ρ_c are the molar mass and density of a crystal. k_R is the surface integration constant. *c* is the species concentration in bulk solution, c_i is the concentration at crystal-solution interface, and c^* is the concentration at equilibrium. In practice, it is difficult to measure the concentration at the interface, c_i (Sobczak, 1990). For industrial applications, c_i is often eliminated and the driving force is considered to be c- c^* , giving an overall crystal growth rate (Balgyda, 2016),

$$G_c = k_G (c - c^*)^g \tag{1.12}$$

where k_G is the overall growth rate constant.



Figure 1.5 Driving force of crystal growth.

1.1.3 Agglomeration and breakup

Particle agglomeration and breakup are the secondary process during reactive precipitation. These processes can occur simultaneously or individually, depending on the force balance between hydrodynamic force and cohesive force (Bubakova *et al.*, 2013; Niu *et al.*, 2019). The hydrodynamic force is originated from the fluid flow around particles. It may be influenced by many factors, such as flow pattern, fluid shear rate, particle shape, and fluid viscosity. While the cohesive force coming from the internal between interacting particles is the sum of electrostatic force, van der Waals force, and other attractive forces. In the case of when the hydrodynamic force dominating, aggregates are created, further developing into closely packed agglomerates. On the contrary, aggregation cannot occur, or the existing unstable aggregates will be broken up due to the exposure to high shear force (Spicer and Pratsinis, 1996; Selomulya

et al., 2001; and Prat and Ducoste, 2006; Caimi *et al.*, 2017; Liu *et al.*, 2018). Particle agglomeration and breakup can be described by the following three steps (Schnebelen *et al.*, 2015; Dizaji *et al.*, 2019). A schematic diagram is illustrated in Figure 1.6.

- Particles collide with each other due to the Brownian movement or the external hydrodynamic force;
- (2) Particles stick together forming loosely packed aggregates under the effect of the internal cohesive force. At this state, aggregates can be easily split with the effect of fluid shear force;
- (3) Aggregates approach each other assembling into closely packed agglomerates as a result of hydrodynamic vortices or crystalline bridges induced by crystal growth.



Figure 1.6 Steps of crystal agglomeration: (a) particle collision; (b) formation of aggregates; and (c) formation of agglomerates, reproduced with permission (Brunsteiner *et al.*, 2005, p.4).

It has been suggested by previous studies that once the chemical condition of reactions is determined, the cohesive force between particles will maintain constant (Bubakova *et al.*, 2013). However, such a force depends on particle

properties, such as particle size, morphology and porosity. Due to the effect of hydrodynamic force on particles, particle properties changes, subsequently leading to the change of cohesive force. Therefore, it is a very big challenge to obtain desired products, as all parameters are not constant during crystallisation process. The major concern is thus how to realise the control of fluid shear.

In recent years, the effect of shear flow on particle agglomeration and breakup has been gradually recognised, aiming to address the effect of stirring intensity of various kinds of reactor on agglomeration kinetics. Serra et al. (1996) investigated the particle aggregation and breakup in a shear flow experimentally, focusing on two parameters, shear stress and particle concentration. They found that shear stress plays an important role in determining aggregate diameter at both laminar flow and turbulent flow, while only for turbulent flow, particle concentration works. Moreover, they observed the same order of magnitude between aggregates and the smallest turbulent eddies, by the estimation from Kolmogorov length scale, $l_{eddy} = (\frac{v^3}{s})^{1/4}$. In Bubakova *et al.*'s (2013) study, they investigated the effect of shear rate on aggregate properties in a Taylor-Couette flow reactor at a steady state. They used an empirical equation based on the torque measurement to characterise the global shear rate of such reactor, giving that $\bar{G} = \sqrt{\frac{2\pi f \tau}{V_B \mu}}$, and they found that the increase of the average shear rate can lead to a narrower size distribution with smaller aggregate size. When the shear rate exceeds a critical value of $G>200 \text{ s}^{-1}$, the change of size can be negligible. In order to quantitatively characterise the dependence of aggregate size on the average shear rate, they derived an empirical equation, expressed as $d_{ave/max} = CG^{-2b}$. More recently, Mayra and Kim (2015) investigated the effect of vortex dimension and intensity on agglomeration process of

Ni_{0.9}Co_{0.05}Mn_{0.05}(OH)₂ particles. They also found that agglomerate size is reduced due to the increase of fluid shear, and the similar expression to the equation in Bubakova et al.'s (2013) study was proposed. In these studies, the average shear rate was employed to characterise the average features of flow field, while the particle size is not constant, often illustrating a distribution around the average value. In fact, for the same value of the average fluid shear rate, its distribution may be extremely different due to the employment of various devices, the configurations, operating conditions. For example, Coufort et al. (2005) investigated the flocculation phenomena in two reactors, the Taylor-Couette reactor and the jar. Not only the mean values of hydrodynamic parameters, i.e., the turbulent kinetic energy dissipation rate and the Kolmogorov length scale, but also their distributions were measured. The result shows that for the same value of mean energy dissipation rate, the agglomerate size in the Taylor-Couette reactor is larger than that in the jar. The authors attributed such difference to the different distributions of the energy dissipation rate. Therefore, they suggested that the mean value of hydrodynamic parameters are not the most significant in determining agglomerate size. However, research from Selomulya et al. (2001, and 2002) reported an opposite result to Coufort et al. (2005), when they used latex particles as an objective. For the similar value of the mean energy dissipation rate, the aggregate size in the mixing tank is about three times larger than that in the Taylor-Couette flow reactor.

From the results of the aforementioned studies, it can be seen that hydrodynamic characteristics have significant effects on the overall process of crystallisation, from the creation of nuclei to the secondary process of particle agglomeration and breakup. However, the use of the average flow dynamic information cannot completely explain the distribution of particle size, as well as various particle morphologies, especially for those reactors with non-homogenous flow fields. Taking into account such variables together, it is difficult to correlate the flow dynamic parameters with resultant particle properties.

1.2 Micromixing and its application

From the mechanism of crystallisation kinetics, it can be seen that supersaturation is the key point to control particle qualities. It is generated by the contact of reactants, while the contact of reactants is dependent on mixing behaviour. The process of mixing is very complicated, as it involves at least three scales, and mixing on individual scales has interaction with each other (Baldyga and Pohorecki, 1995; Mao and Yang, 2017; Lemenand et al., 2017). The large scale mixing, also known as macromixing, signifies the mixing throughout the whole system. It determines the distribution of species concentration for mesomixing, and facilitates fluid flow (Vicum et al., 2003). Mesomixing, with the scale smaller than the integral scale of turbulence, but larger than the Kolmogorov microscale, is related to the inertial-convective diffusion of the disintegrated large eddies (Pohorecki and Baldyga, 1983; Villermaux and David, 1983; Ojaniemi et al., 2018; Luo et al., 2016). It reflects the coarse interaction between the fresh feed with its surroundings (Baldyga and Bourne, 1992). The gradually diminishing plume of fresh feed is followed by micromixing (Baldyga, 1989; and Baldyga et al., 1994). Finally, micromixing is the last stage of turbulent mixing. It represents the process from the viscousconvective deformation of fluid elements to molecular diffusion (Baldyga and Bourne, 1989; Mao and Yang, 2017; Wenzel and Gorak, 2018). The scale of mixing process is illustrated in Figure 1.7. Energy input into the mixing system is dissipated by the viscous deformation of fluid elements, which can be

described in the following four steps (Ottino, 1982; Baldyga and Bourne, 1999; and Johnson and Prud'homme, 2003):

- (1) Fluid elements are conveyed, thus distributed throughout the whole system by bulk convention;
- (2) Daughter vortices are created by inertial-convective diffusion. They will grow and trap new fluid elements;
- (3) Daughter vortices are disintegrated, leading to the formation of a smaller structure by momentum diffusion;
- (4) Chemical reaction occurs ultimately due to molecular diffusion.



Figure 1.7 Mixing process at different scales, reproduced with permission (Johnson and Prud'homme, 2003, p.2265).

From the above introduction to mixing at all scales, it can be seen that macromixing and mesomixing determine the environment for micromixing, as the micromixing occurs at a smaller scale. The mixing on each scale co-exists in one system, having significant effects on the overall precipitation process, while chemical reaction and crystallisation occur at molecular level, which means only micromixing can directly affect its course. On the other word, micromixing plays an important role in the precipitation process. Therefore, the process of micromixing will be discussed in detail in the following sections.

1.2.1 Development of micromixing concept

Danchwerts (1953) proposed the distribution function for residence time, and defined segregation to characterise the efficiency of mixing in a system. Later on, the author pointed out that the distribution of residence time fails to predict the average rate of chemical reaction, as chemical reaction depends on the degree of mixing at the molecular scale (Danchwerts, 1958). Thus, a quantitative definition of the intensity of segregation and its measuring method were given based on the volume fraction of two reactants. By definition, the value of segregation intensity varies from zero to unity, where zero expresses a uniform mixing at the molecular level, while unity denotes a complete segregation of two components. Subsequently, Danchwerts's concept was developed by Zwietering (1959), who defined a life-expectation distribution to describe the extremes of maximum mixedness (i.e., minimum segregation) and complete segregation in a continuous flow system with arbitrary residence time distributions. The schematic diagram of mixing degree is shown in Figure 1.8. More recently, Fournier et al. (1996a), Baldyga and Bourne (1999) introduced the technical terms, macromixing, mesomixing and micromixing, to distinguish different scales of mixing. Furthermore, Kukukova et al. (2009) suggested three separate dimensions, the intensity of segregation, the scale of segregation, and the potential to reduce segregation, to describe mixing co-existing at three scales.



Figure 1.8 Concept of segregation in a case of plug flow reactor: (a) complete segregation; and (b) maximum mixedness, reproduced with permission (Zwietering, pp.7-9).

1.2.2 Micromixing models

In the 1960s, many models were proposed to investigate the degree of micromixing based on the concept of "segregation". The widely accepted three models are the coalescence and redispersion model (Curl, 1963), multi-environment model (Ritchie and Tobgy, 1979; Mehta and Tarbell, 1983a, and 1983b) and IEM model (Villermaux and Devillon, 1972; and Costa and Trevissoi, 1972).

1.2.2.1 Coalescence and redispersion model

The coalescence and redispersion model was proposed by Curl (1963). This model investigates the mixed solution, which is composed of two immiscible liquid phases. It is assumed that all droplets have the same size, and mixing is

triggered from droplets collision, coalescence and redispersion behaviour. The collision rate is set the same for all droplets. Coalescence occurs between two droplets with different concentrations, and the redispersion process takes place immediately, leading to the formation of identical droplets with the same volume concertation. The change of the frequency function of droplet concentration is used to characterise the degree of mixing, where zero represents the complete segregation, while unity represents the maximum mixedness. Other values between zero and unity denotes the intermediate state. However, due to the difficulty in calculating the integro-partial equation of frequency function, the model is simplified by Spielman and Levenspiel (1965), subsequently. They applied the Monte Carlo method to solve the integral equation for such a random coalescence model. In addition, this model fails to include the size distribution and the breakup of droplets, and some complicated interactions were not taken into consideration as well. Moreover, some defined parameters lack physical meaning (Villermaux and David, 1983). Due to these disadvantages, the modelling results deviate from the experimental results to some extent.

1.2.2.2 Multi-environment model

The environment model assumes that for a given system, there are two or more separate environments, and the degree of mixing is either maximum mixedness or complete segregation. Ritchie and Tobgy (1979) developed the equations based on the three-environment model to characterise the effects of micromixing in reactors with two separate feed streams. The flow rate and the residence time distribution of the feed streams can be arbitrary. This model assumes that reactants are unpremixed before entering into the reactor, which means that two feed streams are complete segregation in the entering environment. The separate feed streams are transferred to a maximum mixedness leaving environment. The transfer rate is determined by an environment transfer function, which is proportional to the amount of reactant remaining in the entering environment. A schematic diagram of this model is shown in Figure 1.9. In this model, there are two entering environments for two individual feed streams and only one single leaving environment. Mehta and Tarbell (1983a) refined this model into a four-environment model to overcome some limitations, where the three-environment model is inadequate to describe the competing reaction system. The four-environment model has the same entering environment as in the three-environment model, but it has a separate leaving environment for individual feed streams, and their interaction is included, shown in Figure 1.10. The environment model can describe the complexity in actual chemical reactions, including kinetics of chemical reaction, micromixing, and macromixing together. This advantage makes it acceptable and precise as a general chemical reaction model.



Figure 1.9 Schematic representation of the three-environment model, reproduced with permission (Ritchie and Tobgy, 1979, p.174).



Figure 1.10 Schematic representation of the four-environment model, reproduced with permission (Mehta and Tarbell, 1983, p.323).

1.2.2.3 IEM model

The interaction by exchange with the mean (IEM) model was proposed by Villermaux and Devillon (1972) and Costa and Trevissoi (1972). This model assumes that the reaction system is composed of several effective fluid aggregates and a mean environment. At the micro-scale, fluid aggregates exhibit heterogeneous textures with concentration gradient. Micromixing process causes the deformation of fluid aggregates, and then they will exchange mass with the mean environment, but no interaction with each other appears. Therefore, the micromixing process can be described as the mass transfer process. When mass transfer gradually eliminates the concentration gradient, the whole population has a mean value of concentration, and the maximum mixedness is achieved. On the contrary, if fluid aggregates maintain individually, and no mass exchange occurs, the system is completely segregated. In this model, the micromixing process can be described by the following three stages (Villermaux and David, 1983):

- (1) Distribution of one fluid aggregate;
- Reduction of aggregate size and increase of contact area through laminar starching or turbulent erosion;
- (3) Micromixing by molecular diffusion.

The mass transfer process is suggested to be characterised by micromixing time and the mass transfer coefficient is seen as an indicator for the degree of mixing, where zero denotes complete segregation, and infinity represents maximum mixedness. The value of mass transfer coefficient can be determined by experiment. A defined micromixedness ratio is introduced as a measurement of the degree of segregation.

To summarise, with respect to aforementioned models, empirical parameters are introduced to describe the mixedness of the environment for chemical reaction. However, these empirical models lack the theoretical fundamentals of fluid dynamics or physical meaning, thus, it is hardly applied in practice, especially for complex reaction systems. Also, the predicted results by empirical models sometimes deviate from the experimental data, which limits their applications. Therefore, empirical models were gradually replaced by the theoretical models from the end of 1970s.

1.2.2.4 Diffusion model

The diffusion model was firstly proposed by Mao and Toor (1970), then developed by Nauman (1975) and Ott and Rys (1975). In this model, fluid is divided into some small slabs in a turbulent flow. The size of the slab is assumed to be dependent on hydrodynamic conditions only, which is characterised by the Kolmogorov length scale. The uniform distribution of concentration is ultimately realised by molecular diffusion within these slabs. For mathematic description, the change of reactant concentration is only attributed to the processes of molecular diffusion and chemical reaction, while lacking the effect of convection. Another problem is that the model assumes a constant size of the slab, which is not realistic. Because slabs will be disintegrated and deformed under the effect of turbulence.

1.2.2.5 Lamellar structure model

Due to some drawbacks of the diffusion model, Ottino et al. (1979a, 1980, and 1981), Ranz (1979) and Angst et al. (1982) developed a deformation-diffusion model. This model was then applied to the modelling of the complex interactions for single biomolecular reaction, series-parallel reaction and competitive-parallel reaction respectively by Chella and Ottino (1984). Since the existence of viscosity, fluid elements will deform, creating more surface area to facilitate chemical reaction. Convection term is involved in this model. Fluid elements are assumed to exhibit a lamellar structure with thickness δ_A and δ_B for reactant A and reactant B respectively, shown in Figure 1.11. The mass exchange through molecular diffusion occurs within this structure. Under the effect of fluid deformation, the thickness of these striations $(\delta_A + \delta_B)/2$ decrease, accelerating the diffusion process consequently. This type of deformationdiffusion model is also named after lamellar structure model. While in the case of a spherical-shape fluid element, this model can be called spherical structure model. Due to the consideration of convection term, the mathematical description of this model is expressed as,

$$\frac{\partial c_i}{\partial t} + \boldsymbol{u} \frac{\partial c_i}{\partial x} = D_i \frac{\partial^2 c_i}{\partial x^2} + R_i$$
(1.13)

where u is the velocity vector, D_i the diffusion coefficient, and R_i is the chemical reaction rate. The thickness of striation is used to quantify the state of micromixing. However, mass exchange with the environment is not included in this model, thus errors will be presented (Baldyga and Bourne, 1984a). Another problem is the choice of the reactant lamellar volume, as this model is only applicable for little difference of the lamellar volume to be mixed in a closed system. As one striation approaches infinite thinness, and the other one maintains its initial thickness, it will contradict with the idea of gradually small

thickness due to striation deformation, which means the limiting case cannot be satisfied in this model.



Figure 1.11 Schematic representation of lamellar structure model: (a) an ideal lamellar structure; and (b) instantaneous sectioning of a lamellar structure, reproduced with permission (Ottino *et al.*, 1979, p.878).

1.2.2.6 Diffusion reaction model

Belevi *et al.* (1981), from the same laboratory as Angst, proposed the diffusionreaction model, and they used the competitive, consecutive reaction between alkaline, 1-naphthol solution and diazo salt solution to observe the partial segregation (Bourne *et al.*, 1981a). In this model, a reactant A-rich solution is served as bulk solution, and a small volume of reactant B-rich solution is fed into the bulk solution subsequently. Solution A diffuses into solution B, and all reactions are supposed to occur in solution B. The schematic diagram of this model is shown in Figure 1.12. The shape of the fluid element originating from B-feed stream is assumed to be spherical with a constant radius. This assumption is only reasonable for the deformation rate slower than the reaction rate. Although such assumption will overestimate the effect of diffusion on chemical reaction, it can reduce computational cost at that time. As the size of fluid element is reduced to Kolmogorov microscale, the convection term is ignored. The mass balance of species is given as follows,

$$\frac{\partial c_i}{\partial t} = D_i \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{2\partial c_i}{r\partial r} \right) + R_i \tag{1.14}$$

where r denotes the radial coordinate within the spherical reaction zone.



Figure 1.12 Schematic representation of diffusion-reaction model, reproduced with permission (Belevi *et al.*, 1981, p.1650).

The comparison between the modelling result and experimental result was also conducted (Bourne *et al.*, 1981b, and Angst *et al.*, 1982). It is suggested that the reaction zone is getting smaller than the Kolmogorov scale due to the gradually thinned zone under the effect of laminar shear. However, this model only applies to some particular types of reaction system. Also, the concentration gradient in the bulk solution A is not taken into consideration, which is not consistent with the actual conditions (Baldyga and Bourne, 1984a).

1.2.2.7 EDD model

The engulfment-deformation diffusion (EDD) model, describing the full mechanism of micromixing, was proposed by Baldyga and Bourne (1984b, and 1984c). The idea of this model originates from the spectral analysis of micromixing, introduced by Pohorecki and Baldyga (1983), which indicates the different mechanisms of micromixing at different subranges of eddy size, shown in Figure 1.13. This model assumes three steps involved in micromixing process: engulfment, diffusion and molecular diffusion. Fluid motion causes the generation of vorticity, enabling the engulfment of one fluid element by another. Subsequently, the lamellar structure is formed, illustrated in Figure 1.14. The thickness of these slabs is reduced due to deformation, which is ultimately smaller than the Kolmogorov scale. Such deformation will further lead to the dissipation of kinetic energy. Figure 1.15 (a) displays various steps of the deformation within different subranges. It can be seen from Figure 1.15 (a) (iii) that once the slabs are formed, the concentration gradient increases quickly in the direction of shrinkage, where the molecular diffusion is accelerated consequently. Such diffusion can be simplified into one-dimension behaviour. Finally, molecules encounter each other by diffusion. The whole process can be described by the following equation,

$$\frac{\partial c_i}{\partial t} + u_x \frac{\partial c_i}{\partial x} = D_i \frac{\partial^2 c_i}{\partial x^2} + R_i$$
(1.15)

The velocity at a distance *x* from the centre of the slab is expressed as,

$$u_x = -\Phi_s x \tag{1.16}$$

where Φ_s is the slab deformation rate, which is a function of $(\varepsilon/v)^{1/2}$. Batchelor (1952) gave a more precise expression by assuming elongation-compression kinematics,

$$\Phi_s = C_B \left(\frac{\varepsilon}{\nu}\right)^{1/2} \tag{1.17}$$

where C_B is a constant (0.3-0.5), obtained from experiment. ε is the energy dissipation rate, and *v* is the kinematic viscosity, also provided by experimental data.

The EDD model needs to solve a set of non-linear, parabolic partial differential equations (Equation (1.15)), expressing the unsteady diffusion and chemical reaction within deforming eddies. Also, these equations have to be solved over a period of vortex lifetime. As the vortex dissipates, next generation of vortex will be formed, and the number of the vortex follows an exponential increase. EDD model is similar to the deformation-diffusion model, however, the addition of periodic boundary condition causes the expensive computational cost.



Figure 1.13 Kinetic energy spectrum (ICS: inertial-convective subrange; VCS: viscous convective subrange; and VDS: viscous-diffusion subrange), reproduced with permission (Baldyga and Bourne, 1984b, p.245).



Figure 1.14 Laminated structure of fluid element caused by the effect of vorticity, reproduced with permission (Baldyga and Bourne, 1984b, p.251).



Figure 1.15 Schematic representations of (a) steps of deformation; and (b) action of vorticity acting on fluid elements, reproduced with permission (Baldyga and Bourne, 1984b, pp.252-254).

1.2.2.8 E model

Based on the EDD model, Baldyga and Bourne subsequently simplified it to the engulfment (E) model (Baldyga and Bourne, 1989). E model is valid with a Schmidt number smaller than 4000, where the Schmidt number is defined by the ratio of kinematic viscosity to the molecular diffusivity, as follows,

$$Sc = \frac{v}{D_i} \tag{1.18}$$

This model omits eddy deformation and molecular diffusion. The major contribution comes from eddy engulfment, which is seen as the rate determining step for not too high Schmidt number. In the process of engulfment, the elongated and shrinking slabs are gradually twisted and convoluted under the effect of vorticity, accompanied by the incorporation of fluid elements from its surroundings. The schematic diagram of the stretching of vortex tube and the engulfment process is shown in Figure 1.16. This process will ultimately cause the continuous volume growth of fluid element, which is supposed to follow the exponential law,

$$\frac{dV_{ie}}{dt} = EV_{ie} \tag{1.19}$$

where V_{ie} is the fluid element volume, and *E* is the engulfment rate, which represents the intensity of micromixing, expressed as (Baldyga and Rohani, 1987),

$$E = 0.058 (\frac{\varepsilon}{\nu})^{1/2}$$
(1.20)



Figure 1.16 Schematic representation of the vortex stretching and engulfment, reproduced with permission (Baldyga and Pohorecki, 1995, p.187).

Then, the mass balance equation for a species in the growing reaction volume can be converted to

$$\frac{dc_i}{dt} = E(c_{ie} - c_i) + R_i \tag{1.21}$$

where c_{ie} is the species concentration in the local environment of the growing eddy. Due to this simplification, the partial differential equation is reduced to an ordinary differential equation, thus saving the computational cost. Also, the authors used competitive-consecutive reactions (diazo coupling reaction) to check the accuracy of E model. The result shows that E model exhibits a good agreement with the experimental measurement and EDD model, while with one or two orders of magnitude fast in computational time.

Although the aforementioned two models are still widely used currently, they have some drawbacks. The models assume that the fluid is homogenous and

identical at turbulent condition, while in practice, fluid flow is anisotropic even at a high Reynolds number. However, this is also a big challenge for the computational fluid dynamic modelling of fluid flow. Additionally, either EDD model or E model needs to obtain the value of energy dissipation rate. This value may vary greatly at different fluid flow regions. For instance, the energy dissipation rate in the impeller blade region is two or three orders of magnitude higher than that in other regions. Thus, the use of an average value will deviate from the experimental results to some extent.

1.2.2.9 Incorporation model

The incorporation model was proposed by Fournier and coworkers in 1996 (Fournier *et al.*, 1996a), derived from the earlier work of Villermaux (1990). In this model, two separate fluid streams (fluid 1, and fluid 2) occupy respective environment (Environment 1, and Environment 2) initially. Fluid 2 is divided into many small aggregates, which is progressively invaded by surrounding solution (fluid 1) from Environment 1. This process will lead to the volume increase of fluid 2, so called incorporation, illustrated in Figure 1.17. The volume growth is supposed to follow the law, $V_2 = V_{20}g(t)$, where g(t) is the growing rate. g(t) can be expressed as either a linear or an exponential relationship with time, $g(t) = 1 + \frac{t}{t_m}$, or $g(t) = exp(\frac{t}{t_m})$. The characteristic incorporation time is suggested to characterise micromixing time. Chemical reactions are assumed to take place only within fluid 2, thus the total volume of fluid 2 will not be larger than $V_{10} + V_{20}$. The mass balance for each species is expressed as

$$\frac{dc_j}{dt} = (c_{j10} - c_j) \frac{1}{g} \frac{dg}{dt} + R_j$$
(1.22)

This PhD work adopts the incorporation model due to its simplification, but relatively accurate prediction according to related research work (Schaer *et al.*, 1999; Yang *et al.*, 2005; Chu *et al.*, 2015; Guo *et al.*, 2016; Qin *et al.*, 2017; Ouyang et al., 2018; Li *et al.*, 2019). The calculation of ordinary differential equation can significantly save the computational cost.



Figure 1.17 Schematic representation of the incorporation model, reproduced with permission (Fournier *et al.*, 1996, p.5188).

1.2.3 Characterisation of micromixing efficiency

Several methods have been reported in literature to characterise the mixing performance in chemical reactors, both by physical method and chemical method. These methods can be classified into three main categories, i.e., dilution-based method, monitoring of species concertation, and chemical reaction based method (Aubin *et al.*, 2010). Table 1.1 provides the information of each method for reference.

Characterization	Resulting information	Micro device	Advantages/limitations/associated difficulties	Selected
method		requirements		examples
Dilution of	Qualitative information on	Transparent device	Visualisation of the mixing process is conducted	Hessel et al.,
coloured dyes	mixing quality	or device with	perpendicular to the direction of the flow.	(2003);
	Indirect approximation of mixing time	transparent viewing	Consequently the information obtained is	Schönfeld et
		windows	spatially averaged over the depth of the	al., (2004);
			micromixer. This makes it difficult to distinguish	Wong et al.,
			perfectly mixed systems and complex multi-	(2004); Lee
			layered mixing patterns, and may result in the	et al., (2006)
			measurement of overly short mixing times.	
			Appropriate for mixing in single and two phase	
			systems	

Table 1.1 Summary of experimental methods for characterizing mixing, reproduced with permission (Aubin *et al.*, 2010, p.2067).
Dilution of	Qualitative information on	Transparent device	Using conventional microscopy, the resulting	Knight et al.,
fluorescent	mixing quality	or device with	information is averaged over the depth of the	(1998);
species Indirect approximation of mixing time		transparent viewing window	device. Associated with confocal scanning microscopy,	Johnson <i>et</i> <i>al.</i> , (2002); Stroock <i>et</i>
	3D concentration maps possible		fluorescent dye through the depth of the micro device,	al., (2002);
			3-dimensional concentration data throughout the mixer can be retrieved.Appropriate for mixing in single and two phase systems	Hoffmann <i>et</i> <i>al.</i> , (2006)

Competing		For off-line	For off-line measurements, long time delays	Ehrfeld et
parallel reactions		measurements, there	between sampling from the mixer and sample	al., (1999);
		are no particular	analysis may promote (in certain configurations)	Ehlers
	Quantitative information on	requirements	the secondary reaction if mixing is not complete	et al., (2000);
	the yield of the secondary	For on-line	in the device.	Panic <i>et al.</i> ,
	reaction. The greater the	measurements using	For the Villermaux/Dushman reaction, the	(2004);
	yield of the secondary	UV–Vis	amount of secondary product (iodine) formed	Keoschkerja
	product, the poorer the	spectroscopy, the	depends strongly on the pH of the reacting flow	n <i>et al.</i> ,
	micromixing quality.	measurement cell or	rates used such that the iodine measurements are	(2004);
	No direct information on	the micromixer must	sensitive enough to distinguish different mixing	Nagasawa <i>et</i>
	mixing time is accessible;	be transparent	performances. It is imperative that the same	al., (2005);
	however, mixing time may		reaction conditions are used in order to relatively	Aoki and
	be deduced indirectly from		compare different mixing devices.	Mae (2006);
	the concentration			Kockmann <i>et</i>
	measurements			al. (2006)

			systems	
Monitoring	1-dimensional profiles or 2-	For photometric,	For 1-dimensional concentration profiles, the	Hessel et al.,
species	dimensional maps of species	fluorescence and	measurement is representative of the	(2003);
concentration	concentration, depending on	Raman (using	concentration averaged through the depth of the	Masca <i>et al.</i> ,
	the measurement technique	visible light)	channel or device. It is pertinent only if the flow	(2006);
	used	detection techniques,	structure is 2-dimensional and the concentrations	Salmon et
	Both types of information	the device must be	are constant throughout the depth of the channel.	al., (2005);
	allow the characteristic	optically transparent.	Appropriate for single and two phase systems	Cristobal et
	scale of fluid lamellae in the	For infrared		al., (2006)
	device to be identified,	detection, the device		
	which can be related to	must be transparent		
	mixing time	to infrared radiation		
		wavelengths		

Predominantly used for mixing in single phase

The dilution based method denotes the spreading of a dye with the carrier fluid. The coloured or fluorescent dye is injected into a transparent reactor. Then, with fluid flow, the dye is carried throughout the whole device. This process can be recorded by high-speed camera. Representatives of a blue dye and fluorescein used in experiment is shown in Figure 1.18 and Figure 1.19, respectively. Until the dye evenly distributes in the reactor, the time elapsed is determined as the mixing time. Such time constant can be used to compare mixing performance under different operating conditions. Due to the relatively simple set-up, dilution based method has been widely used in mixing studies (Knight *et al.*, 1998; Johnson et al., 2002; Stroock et al., 2002; Hessel et al., 2003; Wong et al., 2004; Schonfeld et al., 2004; Hoffmann et al., 2006; Lee et al., 2006). However, this method is not applicable for all devices, as the visualisation requires an optically transparent material. Another drawback lies in the determination of the true point for the complete mixing. This means that the homogeneity of the dye spreading in the reactor is determined eyes, which will lead to the artificial error.



Figure 1.18 Observation of a blue dye spreading in a T mixer at different Reynolds numbers, reproduced with permission (Wong *et al.*, 2004, p.367).



Figure 1.19 Observation of fluorescent molecules distributing in the cross section of the channels, reproduced with permission (Stroock *et al.*, 2002, p.649).

The second method, monitoring of species concertation, is the spatial or temporal record of the species concentration in order to calculate the mean value and the coefficient of variance, and thus the mixing efficiency (Hessel *et al.*, 2003). This method is similar to the dilution based method, but the measurement of the species concentration is conducted using photometric detection devices based on colour absorption, fluorescence or luminescence technologies, such as ultraviolet spectroscopy and infrared radiation. For example, the confocal Raman imaging technique was employed by Salmon *et al.* (2005) to observe the local concentration of two liquid streams in a Y-shaped microchannel. Figure

1.20 shows the set-up of the measurement using a confocal Raman microscope. Two liquid streams are chloroform solution and methylene chloride solution, and their concentration maps and the Raman spectra signals are shown in Figure 1.21. Similarly, Masca *et al.* (2006) used the same method to observe the evolution of imidazole concentration in the T-shaped micromixer. This technique has a wider application than the fluorescence-based technique, since not all mixing liquid has an intrinsic fluorescent feature.



Figure 1.20 Set-up of the concentration measurement using a confocal Raman microscope, reproduced with permission (Salmon *et al.*, 2005, p.094106-1).



Figure 1.21 (a) Normalized concentration maps of: (i) chloroform, (ii) methylene chloride, (iii) Sum of the two maps; and (b) Raman spectra signals at three different points, reproduced with permission (Salmon *et al.*, 2005, p.094106-2).

However, it has been realised that the mixing behaviour tested by aforementioned two methods is at the macro-scale, not the same order of magnitude as the micromixing. Therefore, molecular probe based method is more appropriate to characterise the micromixing performance. The third category by employing chemical reaction has been developed quickly and successfully used to characterise the performance of chemical reactors in recent 30 years (Fournier *et al.*, 1996b; and Sudarsan and Ugaz, 2006). A well-performed micromixing test reaction should have the following features (Fournier *et al.*, 1996b):

- (1) Chemical reaction is faster than micromixing;
- (2) Well-known chemical kinetics and characteristic reaction constants;
- (3) Simple test approach with easy measurement of reaction products;
- (4) Stable reaction products with good sensitivity and repeatability;

(5) Low toxicity, safety, and low cost.

The principle of chemical reaction probes lies in the measurement of the yield of by-product produced by the second relatively slow reaction, which is served as an indicator for poor micromixing (Lemenand *et al.*, 2017). A new parameter, segregation index (Xs), is defined and calculated, depending on the concertation of the by-product. Xs ranges from zero to unity, where zero denotes perfect micromixing, and unity represents the total segregation.

There are three main reaction schemes involved in such chemical test method, i.e., single reaction scheme, consecutive competing reaction scheme, and parallel competing reaction scheme. Tables 1.2, 1.3, and 1.4 list the chemical reaction systems involved in each scheme. Due to the lack of the memory of micromixing process and the online measurement of products, the first scheme has been abandoned. The principles of the last two schemes will be described in detail. The representatives for consecutive competing reaction scheme are diazo-coupling of 1-napthol with diazotized sulfanilic acid (Bourne *et al.*, 1981a; and Wenger *et al.*, 1992) and bromination of resorcin (Bourne *et al.*, 1977), and for the parallel competing reaction scheme being alkaline hydrolysis of methyl and ethyl chloroacetate (Yu, 1993), and iodide-iodate method (i.e., Villermaux-Dushman reaction) (Villermaux and Falk, 1994; Fournier *et al.*, 1996b; and Guichardon *et al.*, 2000a and 2000b). The last one, iodide-iodate reaction system is used in this PhD work.

Reference	Reactant A	Reactant B	Reaction rate constant $(m^3 mol^{-1}s^{-1})$	
Keairns and Manning, 1969	Sodium thiosulphate	Hydrogen peroxide	$k_1 = 2.83 \times 10^{-4}$	
Keeler et al., 1965	Ammonium hydroxide	Acetic acid		
Torrest and Ranz, 1970				
Miyairi <i>et al.</i> , 1971				
Mao and Toor, 1971	Hydrochloric acid	Sodium hydroxide	$k_1 = 1.4 \times 10^8$ at 25°C	
	Maleic acid	Sodium hydroxide	$k_1 = 3 \times 10^5$	
	Nitrilotriacetic acid	Sodium hydroxide	$k_1 = 1.4{\times}10^4$	
	Carbon dioxide	Sodium hydroxide	$k_1 = 8.32$	
Methot and Roy, 1973	Sodium thiosulphate	Sodium bromoacetate	$k_1 = 10^{-5}$ at $20^{\circ}C$	
Larosa and Manning,1964	Ethyl acetate	Sodium hydroxide	$k_1 = 1.34 \times 10^{-4}$ at 20°C	

Table 1.2 Reactions of type $A + B \rightarrow R$ showing mixing effects on selectivity, reproduced with permission (Fournier *et al.*, 1996b).

Zoulalian and Villermaux, 1970			
Goto et al., 1975			
Makataka and Kobayashi, 1976			
Aubry, 1972	Nitromethane	Sodium hydroxide	$k_1 = 2 \times 10^{-2}$ at 20°C
Klein et al., 1980			

Table 1.3 Reactions of type $A + B \rightarrow R$, $R + B \rightarrow S$ showing mixing effects on selectivity, reproduced with permission (Fournier <i>et al.</i> ,
1996b).

Reference	Reactant A	Reactant B	Reaction rate constant (m ³ mol ⁻¹ s ⁻¹)
Paul and Treybal, 1971	1-Tyrosine	Iodine	$k_1 = 3.5 \times 10^{-2}$
Bourne and Rohani, 1983			$k_1/k_2 = 9.2$
Zoulalian and Villermaux, 1974	<i>p</i> -Cresol	Iodine	$k_1 = 3.25$
			k ₂ = 1.28 (pH =11, at 24°C)
Zoulalian, 1973	Glycol diacetate	Sodium hydroxide	$k_1 = 5.14 \times 10^{-4}$
Truong and Methot, 1976			$k_2 = 2.27 \times 10^{-4}$ at $25.2^{\circ}C$
Bourne et al., 1977	Resorcinol	Bromine	$k_2 = 10^2$ at 25°C
Nabholz and Rys, 1977	Prehnitene	Nitronium salt	$k_2 = 3 \times 10^{-1}$
	Isodurene		$k_2 = 4 \times 10^{-2}$
	Durene		$k_2 = 10^{-1}$

			$k_1/k_2 > 100$
Bourne et al., 1977	1-Naphthol-6-sulphonic acid	Phenyldiazonium ion	
Bourne and Kozicki, 1977	1,3,5-Trimethoxybenzene	Bromine	$k_1/k_2 = 27$
Bourne et al., 1981	1-Naphtol	Diazotized sulphanilic acid	$k_1 = 7.3 \times 10^3$ $k_2 = 3.5$

Reference	Reactant A	Reactant B	Reactant C	Reaction rate constant $(m^3 mol^{-1}s^{-1})$
Treleaven and Tobgy,	1-Naphthol-6-	4-Sulphophenyl	4-Toluene	$k_1 = 1.83 \times 10^1$
1973	sulphonic acid	diazonium chloride	diazonium chloride	$k_2 = 2.46 \times 10^{-1}$
Miyawaki <i>et al.</i> , 1975	Ammonia	Carbon dioxide	Sodium hydroxide	$k_1 = 4 \times 10^{-1} \text{ at } 25^{\circ} \text{C}$
				$k_2 = 9.3$
Phelan and Stedman, 1981	Hydrazine	Nitrous acid	Hydrogen azide	$k_1 = 6.67$
Paul et al., 1992	Hydrochloric acid	Sodium hydroxide	Organic solvent	
Yu, 1992	Hydrochloric acid	Sodium hydroxide	Ethyl chloroacetate	$k_1 = 1.3 \times 10^8$

Table 1.4 Reactions of type A + B \rightarrow R, C + B \rightarrow S showing mixing effects on selectivity, reproduced with permission (Fournier *et al.*,1996b).

Hydro	chloric acid Sodi	um hydroxide	Methyl	$x_2 = 3.10 \times 10^{-2}$
		cl	hloroacetate	$k_1 = 1.3 { imes} 10^8$
			I	$x_2 = 5.13 \times 10^{-2}$

1.2.3.1 Consecutive competing reaction scheme

The chemical reactions for the consecutive competing reaction scheme can be written in the following formula:

$$A + B \to R \tag{1.23}$$

$$R + B \to S \tag{1.24}$$

Reactants A and B are separately injected into the reactor from individual streams, and their initial stoichiometric ratio is set at 1. The first reaction is much faster than the second reaction. For a perfect micromixing condition, Reactant B is totally consumed by the first reaction, Equation (1.23). On the contrary, for a poor micromixing, the local excessive Reactant B will react with Product R, then by-product S will be detected. A Schematic diagram of the consecutive competing reaction scheme is shown in Figure 1.22. The segregation index, Xs, can be defined as the selectivity of Reactant B, which means the amount of Reactant B involved in the second reaction (Equation (1.24)), calculated from the following equation:

$$Xs = \frac{2n_s}{2n_s + n_R} = \frac{2n_s}{n_{B_0}}$$
(1.25)

where n_{B_0} is the initial mole of Reactant B, n_R and n_S are the net mole of Product R and by-product S, respectively.



Figure 1.22 Schematic diagram of consecutive competing reaction.

1.2.3.2 Parallel competing reaction scheme

The chemical reactions for the parallel competing reaction scheme can be written in the following formula:

$$A + B \to R \tag{1.26}$$

$$C + B \to S \tag{1.27}$$

Reactants A and C are injected together into the reactor from one stream with excessive amount and Reactant B is injected from the other stream, which will be totally consumed at the end of reaction. The first reaction, Reaction (1.26), is instantaneous, and the second one, Reaction (1.27), is fast with the same order of magnitude as the micromixing rate. For a perfect micromixing condition, all of Reactant B is consumed instantaneously by the first reaction, as Reactant B is stoichiometric defect. Therefore, Reaction 2 will not occur, and no by-product

S can be detected. On the contrary, for an incomplete micromixing, Reactant B carried by the fluid element, is unable to be dispersed evenly and disintegrated into molecular scale, then its local excess will induce the occurrence of the second reaction. By-product S will be detected consequently. A schematic diagram of parallel competing reaction scheme is shown in Figure 1.23.



Figure 1.23 Schematic diagram of parallel competing reaction, reproduced with permission (Lemenand *et al.*, 2017, p.460).

It can be seen from the both reactions that according to the stoichiometric ratio, the theoretical amount of Reactant B consumed by the second reaction under the completely segregated condition can be expressed as:

$$Y_{ST} = \frac{n_{C_0}}{n_{C_0} + n_{A_0}} \tag{1.28}$$

where n_{A_0} and n_{C_0} are the initial moles of Reactant A and C, respectively. In practice, the amount of Reactant B consumed by the second reaction should be calculated from the yield of by-product S, as follows,

$$Y = \frac{n_s}{n_{B_0}} \tag{1.29}$$

The segregation index, Xs is defined as

$$Xs = \frac{Y}{Y_{ST}} \tag{1.30}$$

Among these reactions systems listed in Tables 1.2, 1.3, and 1.4, only a few of them are appropriate to be used, since some reactions involve organic or toxic reactants, such as methyl chloroacetate, ethyl chloroacetate and methanol, or some reactions are not fast enough to characterise efficient mixing devices, or products are not stable, and degradation will occur.

As molecular probes, parallel competing reaction scheme shows its advantages in terms of providing a memory of micromixing performance through the concentration distribution of the by-product, since the degree of the micromixing is controlled by turbulent kinetic dissipation rate (Fournier *et al.*, 1996b; and Baldyga and Bourne, 1999; Manzano Martínez *et al.*, 2017). In particular, the iodide-iodate reaction system has been widely used with nontoxic reactants and products, and simple measurement by spectrophotometer, as well as low cost.

It is worth mentioning that particular care should always be taken when comparing the performance under different operating conditions or various reactors, as different values of segregation index may be obtained. This means that the value of *Xs* changes with the choice of the chemical reaction system and the initial reactant concentration. It cannot provide a quantitatively comparative criteria (Baldyga and Bourne, 1990; Baldyga *et al.*, 1998; and Durandal *et al.*, 2006). Thus, it is suggested to use an intrinsic parameter, micromixing time, to evaluate micromixing performance, while the micromixing time can be calculated from the experimental value of *Xs* based on the models mentioned in Section 1.2.2, which will be presented in Chapter 4.

1.2.4 Competition between mixing and chemical reaction

For a reactive precipitation system, the chemical reaction generally takes place extremely fast, almost instantaneously. However, crystallisation including nucleation, crystal growth, agglomeration and breakup is a continuous process. As the supersaturation or reactant distribution can determine final particle size, and its distribution, as well as its morphology (Baldyga and Bourne, 1999; Yang *et al.*, 2018; Shaddel *et al.*, 2019), it is necessary to identify which particular mixing process will directly affect the course of chemical reaction. That means the particle quality is dependent on the relative rate of chemical reaction and mixing.

1.2.4.1 Time scales for chemical reaction

For a nth-order chemical reaction $(nA \xrightarrow{k_n} B)$, the characteristic time constant is

$$\tau_R = [k_n c_{A0}^{n-1}]^{-1} \tag{1.31}$$

where k_n is the rate constant, and c_{A0} is the initial concertation. Such time constant characterises the consumption of half concentration of reactant *A*, indicating the creation rate of supersaturation (Baldyga, 2016).

For the crystallisation process, there is a time period before the formation of the first nucleus, named induction time (or delay time). Induction time is defined as the time elapse from the onset of the contact of reactants to the appearance of the first nucleus in precipitation (Carosso and Pelizzetti, 1984). Nielsen (1964) gave an equation to estimate the induction time, as follows,

$$\tau_N = \frac{6d_m^2 n^*}{D_i lnS} \tag{1.32}$$

where d_m is the molecule diameter, n^* is the number of molecules or ions forming an effective embryo. It can be clearly seen from the above equation that it is impossible to measure the number of molecules in experiment. Dirksen and Ring (1991) proposed an estimation of such period, which is suggested to be inversely proportional to the primary nucleation rate,

$$\tau_N \approx \frac{\kappa}{J} \tag{1.33}$$

where *K* is a constant.

1.2.4.2 Time scales for mixing

At the beginning of Section 1.2, it has been clearly stated that micromixing can directly affect the course of reactive precipitation, while large scale mixing (i.e.,

macromixing and mesomixing) often indirectly influences precipitation process through the change of the local environment for micromixing.

The characteristic macromixing time in a stirred tank reactor with a volume of V_R can be identified with the circulation time (Baldyga *et al.*, 1995; and Torbacke and Rasmuson, 2004), as follows,

$$\tau_{macro} = \frac{V_R}{Q} = \frac{V_R}{ND_R^3} \tag{1.34}$$

where Q is the volumetric bulk flow rate, generated by the agitator, N is the stirred frequency, and D_R is the stirred diameter. More recently, based on the planar laser induced fluorescence (PLIF) technique or particle image velocimetry (PIV) technique, macromixing time can be obtained from experiment with a clear definition that the time is required to achieve a specified degree (generally 95%) of the spatial variance of the tracer concentration from the time at which tracer is injected (Sharp and Adrian, 2001; Kasat *et al.*, 2008; Lehwald *et al.*, 2012; Cheng *et al.*, 2015; Trad *et al.*, 2017; and Taghavi and Moghaddas, 2019). For a sufficiently slow injection of reactant, the uniform composition can be achieved.

Baldyga and Bourne (1984c) suggested that mesomixing, micromixing and chemical reaction take place within different mixing intensities as the reaction zone spreads. Therefore, mixing at both scales is dependent on the distribution of the turbulent intensity and the spatial distribution of the energy dissipation rate, as well as the route of the reaction zone by an appropriate flow map (Wu and Patterson, 1989; Ranade and Joshi, 1990; Bourne and Yu, 1994; and

Ghanem *et al.*, 2014; Zhou *et al.*, 2017). For a coarse-scale turbulent-diffusion mesomixing, Baldyga *et al.* (1993) defined a characteristic length scale, *l_{meso}*

$$l_{meso} = \sqrt{\frac{Q_{feed}}{\bar{u}}} \tag{1.35}$$

where Q_{feed} is the volumetric flow rate of the feeding stream, and \bar{u} is the local mean velocity of fluid flow. A small value of l_{meso} often denotes a local finite feeding source (Baldyga *et al.*, 1993). The time constant at meco-scale caused by turbulent diffusion can be estimated by (Baldyga and Bourne, 1992)

$$\tau_{meso} = \frac{Q_{feed}}{\overline{u}D_i} = \frac{l_{meso}^2}{D_i}$$
(1.36)

For different micromixing models, the characteristic time may be different. The commonly accepted theory is the deformation of fluid elements to Kolmogorov length scale, followed by the molecular diffusion. Therefore, the estimation of characteristic micromixing time is dependent on eddies smaller than Kolmogorov scale. According to Baldyga (1989), such time constant can be estimated by

$$\tau_{micro} = \frac{12}{ln2} \left(\frac{\nu}{\varepsilon}\right)^{1/2}$$
(1.37)

Based on the comparison of these characteristic time constants, including both chemical reaction and mixing, a classification of precipitation was proposed by Baldyga and Bourne (1999). Here, τ_m is used to denote the characteristic time constant related to any mixing process listed above. In the case of $\tau_m >> \tau_R$, chemical reaction is instantaneous, where mixing is the rate determining step,

and for $\tau_m \approx \tau_R$, chemical reaction is fast. If $\tau_m \ll \tau_R$, chemical reaction is slow. The classification of chemical reaction is shown in Figure 1.24 for reference. Mixing plays an important role in the first two cases. According to Baldyga (2016), a chemical reaction can be either considered as a slow reaction when compared to micromixing rate, or classified as a fast reaction compared to the meso- or macro-mixing. This classification is very useful in identifying the model of precipitation, and further scale-up of precipitation process.



Figure 1.24 Classification of chemical reaction, reproduced with permission (Cheng *et al.*, 2012, p.179).

1.3 Chemical reactors and process intensification

The investigation of the effect of mixing on reactive precipitation by models originating from Danckwerts's study, where the author firstly introduced the degree of mixing at the molecular scale (Danckwerts, 1958). From then on, more and more studies have realised the important role of different mixing scales on the course of reactive precipitation, especially in process intensification for the production of functional nanomaterials.

The idea of process intensification derives from last century, and defined by Ramshaw for the first time in the first International Conference on Process Intensification (Ramshaw, 1995). At that time, process intensification was defined as a strategy to reduce the size of chemical plants, but producing desired products at the meanwhile. This definition is quite limited, then Stankiewicz and Moulijn gave a rather clear definition, which is "Process intensification consists of the development of novel apparatuses and techniques that, compared to those commonly used today, are expected to bring dramatic improvements in manufacturing and processing, substantially decreasing equipment-size or production-capacity ratio, energy consumption, or waste production, and ultimately resulting in cheaper, sustainable technologies" (Stankiewicz and Moulijn, 2000). Figure 1.25 shows the components of the process intensification.



Figure 1.25 Components of process intensification, reproduced with permission

(Stankiewicz and Moulijn, 2000, p.24).

Chemical reactor is served as a media to provide mixing environment for chemical reaction. Its performance has been proved to have influences on the final product qualities. Over recent decades, due to the wide application of fine particle materials or even nano-materials in many areas, such as pharmaceuticals, environment, food, and photo catalysis industries, the synthesis of nanoparticles has been attracting extensive attentions. As one of the most efficient approach in producing fine particle materials, reactive precipitation is promising, while this process generally requires an improvement of the performance for the conventional reactors in terms of mixing, mass transfer, and heat transfer. Thus, the technique for process intensification is necessary. As can be seen from Figure 1.25, the intensification can be realised by the change of operating condition, the development of new equipment, and the modification of apparatus configuration. Over recent decades, various reactors have been developed and adopted to achieve this goal, such as stirred tank reactor (Cheng et al., 2016; Hua et al., 2017; and Baronas et al., 2019), spinning disk reactor (Farahani et al., 2017; Vilardi et al., 2017; and Jahanshahi-Anboohi et al., 2019), rotating packed bed reactor (Chen et al., 2003; Lin et al., 2016; and Fan et al., 2016), impinging jet reactor (Wu et al., 2007; Valente et al., 2012; and Kugler et al., 2016), and vortex reactor (Marchisio et al., 2009; Santillo et al., 2012; and Bensaid et al., 2014).

1.3.1 Stirred tank reactor

As one of the conventional chemical reactor, stirred tank reactor has been successfully applied into reactive crystallization process over last several decades (Taghavi *et al.*, 2011). A typical structure of the stirred tank reactor is depicted in Figure 1.26. Numerous theoretical and experimental research work

has been reported about the investigation of the effects of operating parameters and reactive conditions on the course of precipitation or on the product properties. For example, Pohorecki and Baldyga (1985) prepared barium sulfate particles in a continuous stirred tank reactor with different stirring speeds. They attributed the increase of particle size with stirred speed to the enhanced turbulent micromixing. Spicer *et al.* (1998) investigated the effect of shear on particle properties in a flocculation process, and they found that shear can reduce particle size and enables a compact structure. In Jung *et al.*'s (2010) study, they simultaneously synthesized two types of morphology of calcium carbonate particles in a stirred tank reactor. They suggested that this phenomenon is caused by the local non-homogenous distribution of the mixing intensity.



Figure 1.26 Schematic representation of a stirred tank reactor, reproduced with permission (Duan *et al.*, 2018, p.680).

With the investigation of the stirred tank reactor both in experimental work and theoretical modelling, some drawbacks have gradually emerged. One

configuration is not applicable for multiple applications (Mavros, 2001). The conventional stirred tank reactor with a non-homogenous flow field, shown in Figure 1.27, is not beneficial to the formation of stable products. For example, the capability of the agitator is to induce the circulation of fluid, and avoid the damage of species in the reactor, such as crystals, biological cells, which are often shear-sensitive (Spicer et al., 1996; Ducoste et al., 1997; and Justen et al., 1998). Raghav Rao and Joshi (1988) found that the employment of a pitched turbine downflow (PTD) typed impeller is more efficient in terms of power consumption and mixing time, when compared to disk turbine (DT) and pitched turbine upflow (PTU). Another type of impeller, Rushton impeller with a high mass transfer coefficient has been widely used since 1950s (Nienow et al., 1996). However, it also has some drawbacks, such as uneven distributed shear stress, and low axial pumping capacity (Yang et al., 2015). Various modifications have been developed in literature, such as the change of blade (Bujalski et al., 1990; Albiter et al., 1994; and Yoon et al., 2001), as well as its assembling height (Kong et al., 2012), the number of impeller (Sanchez et al., 1992; Jaworski et al., 2000; and Yang et al., 2015), and the addition or removal of baffle (Lu et al., 1997; Haque et al., 2006; and Assirelli et al., 2008).



Figure 1.27 Schematic representation of a standard Rushton-turbine flow pattern, reproduced with permission (Mavros, 2001, p.114).

The application and improvement of the conventional stirred tank reactor still remains a challenging work due to its relatively intrinsic complexity of the flow pattern. The development of other kinds of reactor is necessary to meet various demands in industrial process.

1.3.2 Spinning disk reactor

The spinning disk reactor works by the rapid rotation of disk, then centrifugal force is imposed to the fluid flowing through its surface. The configuration of a typical spinning disk reactor is shown in Figure 1.28. Due to the acceleration imposed to fluid, the typical thin wavy film with a thickness of 50 to 500 μ m and a high surface area to volume ratio of up to 30000 m²/m³ can be formed on the disk surface (Boodhoo, 2013). These features enable the creation of high supersaturation, which is beneficial to the induction of reactive precipitation (Boodhoo and Al-Hengari, 2012).



Figure 1.28 Schematic representation of the spinning disk reactor, reproduced with permission (Wang *et al.*, 2017, p83).

Many studies have applied spinning disk reactor to prepare various particles, and compared with the conventional stirred tank reactor, such as curcumin nanoparticles (Tai, *et al.*, 2007; and Khan and Rathod, 2014), barium sulfate particles (Dehkordi and Vafaeimanesh, 2009; and Jacobsen and Hinrichsen, 2012), titanium dioxide particles (Mohammadi *et al.*, 2014), and Fe₃O₄ nanoparticles (Chin *et al.*, 2008). It is suggested by Cafiero *et al.* (2002) that the power consumption of producing a specific number of crystals in the spinning disk reactor (115 W/kg with 4×10^{9} /cm³) is much lower than that in a conventional continuous stirred tank reactor (110 W/kg with 3×10^{8} /cm³). In the study of Jacobsen and Hinrichsen (2012), they observed controllable barium sulfate particle size in their experiment by changing process parameters, such as disk structure and rotational speed, shown in Figure 1.29(a). They attributed such a good particle quality to the high and controllable micromixing efficiency created by the spinning disk reactor, shown in Figure 1.29 (b). Mohammadi *et al.* (2014) has carried out a series of experiment with a wide range of operating

conditions to synthesize titanium dioxide particles, and they used response surface method to obtain the optimized experimental condition by considering particle size and yield. It was found that particles are about at least 2 orders of magnitude smaller in size than those prepared in the conventional stirred tank reactor, and the particle size distribution, shown in Figure 1.30, is narrower with the increase of the disk rotational speed. Moreover, the modification of the disk surface has been suggested effectively to intensify the particle formation process due to the change of smooth film to wavy film. Aoune and Ramshaw (1999) found that the mass transfer rate in the wavy film is about 9 time higher than that in a smooth film, and the heat transfer rate is 5 time higher, which is an improvement for reactive precipitation process.



Figure 1.29 Change of (a) barium sulfate particle size; and (b) micromixing efficiency at different disk rotational speeds in the spinning disk reactor, reproduced with permission (Jacobsen and Hinrichsen 2012, pp.11648-11650).



Figure 1.30 Particle size distribution at different disk rotational speeds in the spinning disk reactor, reproduced with permission (Mohammadi *et al.*, 2014, p.176).

However, the spinning disk reactor has a disadvantage of fouling or plugging on disk surface, shown in Figure 1.31. Such fouling is adverse to heat or mass transfer process, or even reduce the lifetime of the reactor. In order to prevent the occurrence of the fouling, surface coating method has been adopted, such as Teflon (Oxley *et al.*, 2000).



Figure 1.31 Severe fouling in spinning disk reactor in the spinning disk reactor, reproduced with permission (Wang *et al.*, 2017, p84).

Another two similar devices to the spinning disk reactor are the spinning core reactor and the rotating packed bed reactor. The rotating segment in the spinning core reactor is changed to a cone, shown in Figure 1.32, leading to the centrifugal force not align to the cone surface (Hetherington and Jachuck, 2001). In contrast to the spinning disk or cone reactor, the rotating packed bed reactor is composed of an enclosed system packed with structured packings, shown in Figure 1.33. Over recent years, high-gravity or hyper-gravity technology is used in the rotating packed bed reactor to demonstrate the advantages in terms of particles control, high product yield with reduced cost (Chen *et al.*, 2000; Chen and Shao, 2003; and Rao *et al.*, 2004; Wu *et al.*, 2018; Cao *et al.*, 2019).



Figure 1.32 Schematic representation of the spinning cone reactor, reproduced with permission (Wang *et al.*, 2017, p84).



Figure 1.33 Sketch of the rotating packed bed (RPB) unit: (a) horizontal-axis RPB; and (b) vertical-axis RPB. Legend: 1: liquid feed inlet; 2: liquid outlet; 3: vapor inlet; 4: vapor outlet; 5: packing; and 6: motor, reproduced with permission (Rao and Goswami, 2004, p.1150).

1.3.3 Impinging jet reactor

The impinging jet reactor is based on the continuous injection of two individual streams from the opposite directions. A schematic diagram is shown in Figure 1.34, and the typical flow pattern is shown in Figure 1.35. It can be seen that one stream encounters and impinges against the other stream in reactive cavity, where extremely high fluid velocity will be created and the mixing occurs under strong turbulence. The impinging jet reactor has attracted many attentions in recent years due to its major advantage, i.e., fast formation of high mixing intensity. Since the mixing volume is confined, a homogenous supersaturation profile can be quickly achieved before the onset of nucleation (Midler Jr *et al.*, 1994; Mahajan and Kirwan, 1994; Johnson and Prud'homme, 2003; and Stahl *et al.*, 2001). It has been suggested by Siddiqui *et al.* (2009a) that the mixing

intensity, or the local energy dissipation rate in the impinging jet reactor, ranging from 20 W/kg to 6800 W/kg at the flow rates ranging from 40 mL/min to 500 mL/min, is several orders of magnitude higher than that in the conventional stirred tank reactor. Thus, this device has been widely used in both organic and inorganic particle preparation (Johnson, 2004; and Marchisio *et al.*, 2006; Baber *et al.*, 2016; Wojtalik *et al.*, 2020), especially in pharmaceutical process (Lindrud *et al.*, 2001; Crawford *et al.*, 2003; Paul *et al.*, 2005; Tung *et al.*, 2009; and Tung, 2013).



Figure 1.34 Schematic representation of the impinging jet reactor, reproduced with permission (Siddiqui *et al.*, 2009, p.41).



Figure 1.35 Flow pattern in a round impinging jet reactor, reproduced with permission (Tamir, 2014, p.59).

The research work of Mahajan and Kirwan (1996) has indicated that the key point to control the reactive precipitation in the impinging jet reactor is dependent on Reynolds number, and the effective condition relies on the micromixing time to be shorter than the mean residence time. Jiang et al. (2015) employed a dual imping jet mixer to synthesize drug crystals at different jet velocities. Particle size becomes smaller, and its distribution is narrower when increasing the inlet velocity, shown in Figure 1.36. Also, it can be seen that particle size distribution changes into unimodal distribution from bimodal distribution, indicating a more uniform particle quality. In order to quantify the relationship between the average particle size and hydrodynamic conditions, a fitting line based on power-law function is obtained, shown in Figure 1.37. Such a fitted curve can be used to obtain desired particle size without experiment. The authors suggested that a short residence time and high energy input lead to the increase of nucleation rate, and the particle growth rate is thus relatively low. Moreover, the energy created in the cavity is sufficiently high to avoid particle agglomeration (Wang et al., 2017).


Figure 1.36 Particle size distribution in a confined Y-shaped dual imping jet mixer at jet velocities at 15 m/s (green);10 m/s (red); 2.5 m/s (blue); and 1.1 m/s (pink), reproduced with permission (Jiang *et al.*, 2015, p.246).



Figure 1.37 Fitting of crystal size and Reynolds number, reproduced with permission (Jiang *et al.*, 2015, p.246).

Further intensification of the reactive process in the impinging jet reactor can be realised by the combination with other reactors. Fan et al. (2016) combined the impinging jet reactor with a rotating packed bed reactor to synthesize Fe₃O₄ nanoparticles by co-precipitation method. The obtained particle size is extremely small, ranging from 7.5 nm to 11.3 nm. Siddiqui et al. (2009b) also employed an imping jet reactor combined with a sonication probe to prepare Fe₃O₄ nanoparticles. They found that the size of Fe₃O₄ agglomerates greatly drops and the size distribution is much broader with the additional treatment with sonication, shown in Figure 1.38. They suggested that the decreased size is attributed to the dispersion of soft agglomerates, caused by the ill-formed hard agglomerates, while those well-formed hard agglomerates are still closely bonded, resistant to shear force and sonication, thus, the both contrary effects lead to a broad size distribution. Then, the authors adopted the iodide-iodate reaction system to validate the mixing efficiency and CFD simulation to calculate the turbulent energy dissipation rate, shown in Figure 1.39. It is found that at high flow rate, the sonication treatment has limited effect on particle formation. It is known that, high inlet velocity guarantees the fast formation of mixing intensity, which is the major advantage of the impinging jet reactor. However, for this study, a strong turbulent condition and high mixing intensity lead to undesired results. Thus, it can be deduced that not all plausible intensified treatments are necessary, and the balance between the forces exerting on particles and their intrinsic forces should be carefully considered.



Figure 1.38 (a) Change of particle size with feed flow rate; and (b) Particle size distribution with the treatment of sonication in the impinging jet reactor, reproduced with permission (Siddiqui *et al.*, 2009b, p.42).



Figure 1.39 Variation of energy dissipation rate in (a) axial direction; and (b) radial direction at various flow rate in the impinging jet reactor, reproduced with permission (Siddiqui *et al.*, 2009b, p.42).

1.3.4 Micro-reactor

Micro-reactor is the miniaturised reactor compared to the conventional chemical reactors. It is often composed of a set of small channels with size in the order of micrometre (Doku et al., 2005), shown in Figure 1.40. This device has attracted many attentions and developed quickly over recent decades since the "International Conference on Micro-reaction Technology" held in 1997 (Chen et al., 2008). Due to small in size, micro-reactor is portable and flexible with low reactant consumption (Doku et al., 2005). Thus, it has the potential to realise the continuous operation, which has demonstrated many advantages compared to the batch processing, in terms of controlling the selectivity, saving production time, and diminishing safety issues (Fan et al., 2008; and Takebayashi et al., 2012). McCarthy et al. (2007) prepared barium sulfate particles in a narrow channel reactor with continuous operation. They investigated various parameters, including channel velocity, dimension, residence time and supersaturation, and the result indicates a reduced particle size with the increase of channel velocity. When compared to the conventional stirred tank reactor, in which the particle size is about 3 µm, they observed a smaller particle size of 0.2 µm with a narrower size distribution in the microchannel reactor, shown in Figure 1.41. They also found that the hydrodynamic conditions have significant effect on particles, where high velocity facilitates the formation of special particles. In order to explain such result, they compared various length scales of turbulent mixing, shown in Table 1.5, and suggested that high levels of micro-mixing and convective mass transfer are rather easy to be achieved with a narrow channel, intensifying crystallisation process. Similar result of 15% size reduction of copper chromite nanoparticles by employing micro-reactor was also observed in Appalakutti et al.'s study (2015). In the study of Chen et al. (2005), they analysed the important role of mixing on the

protein nucleation in a micro-fluidic channel. Another work by Trippa and Jachuck (2003) also investigated the effect of mixing on the course of calcium carbonate particles in narrow channel reactors. They used a flow visualisation technique, recorded by a digital camera to observe mixing behaviour. They found that mixing of the reactant can influence the development of superstation in the channel, which then affects the kinetics of the nucleation and particle growth.



Figure 1.40 Schematic representation of a typical micro-reactor, reproduced with permission (Appalakutti *et al.*, 2015, p.30).



Figure 1.41 Barium sulfate particle size distribution in the micro-channel reactor and stirred tank reactor, respectively, reproduced with permission (McCarthy *et al.*, 2007, p.78).

Time/length scale	Expression		Units	Range of parametric values corresponding to 62 < Re < 1025
Energy dissipation, ε_{turb}	$\varepsilon_{\text{turb}} = \frac{Q\Delta P}{\rho V} = \frac{2fV^3}{d_h} \text{ for } 4f = 0.316 \text{ Re}^{-0.25}$	(11)	Wkg ⁻¹	0.001–482
Inertial-convection, τ_s	$\tau_s = \frac{3}{4} \frac{R^{0.66}}{\varepsilon_{\rm turb}^{0.33}}$	(12)	ms	75.0–0.38
Micro-mixing (Kolmogorov), τ_E	$\tau_E = \frac{1}{E} = 17.24 \left(\frac{\nu}{\varepsilon_{\text{turb}}}\right)^{0.5}$	(13)	ms	545.0-0.78
Molecular diffusion (Batchelor), $\tau_{\rm diff}$	$\tau_{\rm diff} = \frac{\eta_B^2}{D}$	(14)	ms	32.0-0.05
Kolmogorov length scale	$\eta_k = \left(\frac{\nu^3}{\varepsilon_{\rm turb}}\right)^{0.25}$	(15)	μm	178.0–6.7
Batchelor length scale	$\eta_B = \eta_k \mathrm{Sc}^{-0.5}$	(16)	μm	1.78–0.067

Table 1.5 Characteristic time and length scales of turbulent mixing, reproduced with permission (McCarthy et al., 2007, p.81).

Another advantage of micro-reactor is that it can provide high surface area densities, compared to the conventional stirred tank reactor, which is beneficial to heat or mass transfer during chemical reactions (Trippa and Jachuck, 2003). Takebayashi *et al.* (2012) employed a gas-liquid micro-reaction system for the synthesis of isocyanate. The products show a better quality with no impurities and higher yield, compared to those from batch reaction. The authors attributed such result to the efficient gas-liquid mass transfer in the micro-flow system, thus the improved interfacial area per unit volume, which is difficult to be realised in the conventional macro and batch process. Fan *et al.* (2008) used TiO₂ nanoparticles dispersed in ethylene glycol to investigate to heat transfer in a micro-heat exchanger. Due to such compact structure, the reactor shows a quick dynamic response, and the overall heat transfer coefficient is enhanced up to 35% compared to the conventional heat exchanger.

To summarise, the aforementioned reactors have their individual advantages, and can be applied to particle preparation process with various purposes. Further improvement of these reactors and the development of novel reactors are still necessary in order to meet the increasing requirements in different fields, such as cell cultivation, drug synthesis, particle classification, water purification, and slurry filtration.

1.4 Taylor-Couette flow reactor

1.4.1 Introduction to Taylor-Couette flow reactor

Taylor-Couette flow (TC) reactor consists of two co-axial cylinders, where the inner cylinder rotates relatively to the outer cylinder in a working mode. The

typical flow, generated in the gap area has long been a subject of interest in fluid mechanics over 100 years due to several reasons (Wang *et al.*, 2015; and Grossmann *et al.*, 2016), as follows,

- This system has a simple configuration with high symmetries, which enables the experimental measurement;
- (2) It is one of the paradigmatic systems, which is well-defined by the Navier-Stokes equations;
- (3) The global balance between driving force and dissipation can be derived;
- (4) This system enables fundamental studies, such as the development of boundary layer.

Therefore, numerous theoretical studies based on the TC system have been conducted, including the onset of instabilities (Taylor, 1923; DiPrima and Swinney, 1981; and Tuckerman, 2014), transition of flow pattern (Andereck *et al.*, 1986; Boubnov *et al.*, 1995; and Bodenschatz *et al.*, 2000), and turbulence (Lathrop *et al.*, 1992; Dong, 2007; and Huisman *et al.*, 2014).

The prototype of the TC device was designed by a French physicist, Maurice Couette, whose initial purpose was to estimate the viscosity of the fluid by measuring the torque of the inner cylinder (Couette, 1890). Since torque is theoretically proportional to $\omega \times v$, Taylor described the stability of fluid flow mathematically by solving a set of partial differential equations and observed the unstable flow by the ink visualisation for the first time (Taylor, 1923). Furthermore, Taylor successfully measured the velocity distribution of the fluid at various radius ratios and Reynolds members by intrusive electrical measurement for two cases: (a) inner cylinder rotating with fixed outer cylinder;

(b) outer cylinder rotating with fixed inner cylinder, and suggested that there is a critical value for the transition of fluid from steady state to turbulent flow (Taylor, 1936).

The general configuration of the TC device is shown in Figure 1.42. The flow generated in the gap area based on the relative motion of both co-axial cylinders can be classified into different flow patterns from laminar flow to turbulent flow, and such classification is suggested to be quantitatively characterised by Reynolds number or Taylor number, defined by,

$$Re = \frac{r_i \omega(r_o - r_i)}{\nu} \tag{1.38}$$

$$Ta = \frac{r_i \omega^2 (r_o - r_i)^3}{\nu^2} = Re^2 \frac{(r_o - r_i)}{r_i}$$
(1.39)

where r_o and r_i are the radius of the outer cylinder and inner cylinder, respectively. At a very low Reynolds number, the flow is laminar Couette flow (CF), shown in Figure 1.43(a). There is a critical point, where the azimuthal Couette flow becomes unstable, and the counter-rotating toroidal vortices appear in pairs. The flow transforms into laminar Taylor-vortex flow (LTVF). This means a series of instabilities caused by the centrifugal force will appear when the Reynolds number exceeds the critical value, including laminar Taylor-vortex flow (LTVF), wavy Taylor vortex flow (WVF), modulated wavy vortex flow (MWVF) (including two different modes, i.e., singly periodic wavy vortex flow (TTVF), and finally the fully developed turbulent Taylor vortex flow (Taylor, 1923; Gorman, M. and Swinney, 1979, and 1982; Fenstermache *et al.*, 1979; Swift *et al.*, 1982; Shaw *et al.*, 1982; and Coughlin *et al.*, 1991). At the last flow pattern, the vortex loses its structure, becoming indiscernible (Smith

and Matsoukas, 1998). Figure 1.43 displays the flow visualisation at different Reynolds numbers. More specifically, in the case of the independent rotation of both cylinders, the distribution diagram of flow pattern according to independent Reynolds numbers of both inner cylinder and outer cylinder is displayed in Figure 1.44.



Figure 1.42 Configuration of the TC device, reproduced with permission (Richter *et al.*, 2009, p.2385).



Figure 1.43 Flow pattern at different Reynolds numbers: (a) CF; (b) LTVF; (c) WVF; (d) MWVF; and (e) TTVF, reproduced with permission (Fenstermacher *et al.*, 1979, p.128; and Richter *et al.*, 2008, p.3508).



Figure 1.44 Flow pattern with independently rotating cylinders in a Taylor-Couette system at a radius ratio of 0.833, reproduced with permission (Grossmann *et al.*, 2016, p.55).

Additionally, it is worth mentioning that such critical value at the onset of the instability depends on both the radius ratio and the fluid property, while the size and number of the vortex is only dependent on the aspect ratio (DiPrima *et al.*, 1984; and Dutta and Ray, 2004). The radius ratio and the aspect ratio of the TC device are defined by Equations (1.40) and (1.41), respectively.

$$\eta = \frac{r_i}{r_o} \tag{1.40}$$

$$\beta = \frac{L_R}{r_o - r_i} \tag{1.41}$$

where L_R is the length of the TC device.

Compared to the conventional stirred tank reactor, the TC device has many advantages. The typical counter-rotating toroidal vortices can lead to a large specific surface of the device (Baier *et al.*, 2000; and Richter *et al.*, 2008). Due to the fluid viscosity, fluid shear is an important part in determining hydrodynamic environment. It has been suggested that the shear rate distribution is narrow with the absence of high shear regions in the TC reactor (Soos *et al.*, 2007), while for the stirred tank reactor, the shear rate near the impeller is several orders of magnitude higher than other regions. Also, the flow pattern in the TC device is easily controlled by adjusting the rotational speed of the inner cylinder (Li *et al.*, 2015). This device can be seen as a promising technology to be applied to many engineering processes.

1.4.2 Application of TC reactor

Due to the aforementioned advantages of the TC reactor, extensive interest has been raised in many fields. For different purposes, different features of the TC reactor will be favoured, such as mass transfer, shear stress, heat transfer, and centrifugal force. Also, the TC reactor has shown its high flexibility in terms of process design and operating mode, including combination with other reactors, multiple feeding inlets and outlets, continuous operation, and recirculation of products. For example, Figure 1.45 demonstrates various feeding modes of the TC reactor used for the crystallisation of guanosine 5-monophosphate (Nguyen *et al.*, 2012). All these evidences indicate that the TC reactor is a promising device with multiple applications.



Figure 1.45 Multiple feeding modes of the TC crystallizer: (a) feeding mode I; (b) feeding mode II; (c) feeding mode III; (d) feeding mode IV (1: methanol antisolvent solution; 2: GMP feed solution), reproduced with permission (Nguyen *et al.*, 2012, p.2782).

1.4.2.1 Crystallisation

In recent twenty years, the application of the TC reactor in the field of crystallisation has drawn increased attention (Kim *et al.*, 2014). Many studies have demonstrated the effect of the unique Taylor vortex on the course of particle formation. In particular, Kim's group has expanded the application of the TC reactor to preparation of various kinds of particles, including calcium carbonate (Jung *et al.*, 2000, and 2010; and Kang *et al.*, 2003), barium sulfate (Aljishi *et al.*, 2013; Liu *et al.*, 2020), guanosine 5-monophosphate (Nguyen *et al.*, 2010, 2011, and 2012), L-lysine (Nguyen *et al.*, 2017), and Ni-rich hydroxide (Kim *et al.*, 2011; Thai *et al.*, 2015; Mayra and Kim, 2015; and Kim and Kim, 2017).

In a gas-liquid reaction system, a good example is the preparation of calcium carbonate particles from carbon dioxide gas and calcium hydroxide solution. According to Kang et al.'s (2003) study, they observed three types of morphology of calcium carbonate crystals, i.e., rhombohedron, spindle and needle. In order to explain this transition, they proposed a "shape criterion", and correlated it with operating conditions. They found that with increasing the rotational speed of the inner cylinder, the interfacial transport of carbon dioxide is enhanced. The main contribution comes from the high shear rate of the Taylor vortex. The strong shear force exerting on bubbles will considerably reduce their size, then increasing interfacial area, and mass transfer rate. Also, Jung et al. (2000) compared this reaction system with the traditional Mixed Suspension-Mixed Product Removal (MSMPR) crystallizer. A relationship of mass transfer coefficient and wall shear stress is shown in Figure 1.46. In MSMPR crystallizer, the mass transfer process to the gas-liquid interface is limited, due to the sparsely dissolved feature of the carbon dioxide in water. This means the mass transfer rate is quite slow, which will limit the nucleation and crystal growth. As can be seen from Figure 1.47, particles are smaller in size and more uniform with single morphology when employing the TC reactor. The flow dynamic property is non-homogenous in the MSMPR crystallizer, where the turbulent intensity is much higher around the vicinity of the impeller, while decreasing quickly away from the impeller. Dluska et al. (2004) measured the specific interfacial area in a gas-liquid system, and they found it is one order of magnitude higher in the TC reactor than that in a stirred tank reactor.



Figure 1.46 Relationship between mass transfer coefficient and wall shear stress, reproduced with permission (Jung *et al.*, 2000, p.736).



Figure 1.47 Calcium carbonate (a) particle size distribution; and (b) mprphologies at (i & ii) TC reactor, and (iii & iv) stirred tank, reproduced with permission (Jung *et al.*, 2010, p.3335).

In a liquid-liquid reaction system, barium sulfate particles often serve as a model substance to investigate the effects of various parameters. The reactants are generally barium chloride solution and sodium sulfate solution. As mentioned before, the flow pattern in the TC reactor presents a series of instabilities with the increase of Reynolds number. Aljishi *et al.* (2013) investigated the preparation of barium sulfate particles before and after the critical flow transition point. In laminar flow region without the effect of vortex, there is no clear trends in crystallize size, while when the vortex appears, particles get smaller in size, and size distribution is narrower. The author suggested an important role of vortex motion in determining particle structure and morphology. However, they failed to quantitatively explain the interaction between hydrodynamics and crystallisation.

1.4.2.2 Granulation

Granulation generally refers to the modification of already formed solid particles, such as aggregation or agglomeration, coagulation and breakup. Wang *et al.* (2005) investigated the aggregation and breakup of the spherical latex particles in a TC flow in experiment. In order to observe particles, they employed a progressive scan monochrome CCD camera. Furthermore, they also used computational fluid dynamics coupled with quadrature method of moments (QMOM) to predict particle size distribution. Both experimental and modelling results suggest the great effects of local shear rate on the aggregation and breakage. Krishnaraj and Nott (2016) found a puzzling phenomenon when processing granular solid materials in the TC device that all components of the shear stress rise nearly exponentially with depth. They attributed this phenomenon to the transformation of the single toroidal vortex, which spans the entire cell with the addition of solid phase, while the vortices remain their original size with the addition of liquid or gas phase. Their study provides an insight into the consideration of the inverse-effect of particles on fluid flow.

1.4.2.3 Particle classification

Particle classification is the key technique to obtain uniform particles in size, which will then affect particle rheological behaviour or other properties. In most cases, the density difference of these particles from fluid is very small, however, shear-induced particle migration under the influence of Taylor vortices can be a promising approach to classify particle size. Ohmura et al. (2005) has successfully realised the classification of particles with an initially wide size distribution, both numerically and experimentally. They used a wide range of particle size from 10 µm to 80 µm, and observed that large particles (about 50 μm to 80 μm in size), which are located near the edges of Taylor vortex tend to be transported downward or upward due to the bypass flow effect, while small particles (about 20 µm to 50 µm in size) are mainly remained in the core of vortices, shown in Figure 1.48. Especially, when an axial flow is superimposed to the Taylor vortex flow, the by-pass flow effect can be enhanced. Similarly, Kim et al. (2013) obtained such result by using computational fluid dynamics method, where large particles quickly pass through the vortices, while small particles are trapped in the core. However, the difference with Ohmura et al.'s (2005) result is that when particles loaded into the TC reactor exceeds the capacity of the vortex, even small particle will escape from the core, and move with bypass flow. Moreover, large particles tend to fall to the bottom with the effect of gravity, and small particles move to the top, shown in Figure 1.49. A further study of particle motion in a Taylor vortex was conducted by Qiao et al. (2015). They focused on the difference of particle density, rather than particle size. Their results show four different particle trajectories for light particles with the increase of the inner cylinder rotational speed, shown in Figure 1.50, while heavy particles only presents two trajectories. The main reason may be due to

the difference of dominating force acting on particles, such as pressure force, and centrifugal force. These findings provide a good understanding of the interaction mechanisms between particles and vortices, which is beneficial to particle classification.



Figure 1.48 Particle motion under the effect of Taylor vortex, reproduced with permission (Ohmura *et al.*, 2005, p.70).



Figure 1.49 Particle distribution in the TC reactor, reproduced with permission (Kim *et al.*, 2013, p.109).



Figure 1.50 Four typical light particle trajectories at different Reynolds number of (a) Re=95; (b) Re=123; (c) Re=136; and (d) Re=150, reproduced with permission (Qiao *et al.*, 2015, p.123).

1.4.2.4 Cell cultivation

Due to the growing field of bioengineering and its applications, much attention has been paid to the tailored cell cultivation based on the different growth environment by employing bioreactors. Compared to the conventional stirred tank, which may induce high turbulent shear near the impeller, harmful for cell growth, TC reactor shows its advantages in terms of mild shear and effective mass transfer, and has been commercialized by Synthecon (Haut *et al.*, 2003; and Tanzeglock, 2008).

The main concern of cell cultivation is the oxygen transport, which is a critical factor during cell growth. Haut *et al.*'s (2003) investigated the mass transfer of oxygen under both wavy vortex flow and turbulent Taylor flow. The results show that TC reactor can ensure a uniform distribution of oxygen throughout the whole volume by testing the oxygen uptake rate. More precisely, Curran and Black (2005) measured the dissolved oxygen concentration in the TC reactor, and calculated the mass transfer coefficient. They found that the available oxygen even exceeds the consumption by murine fibroblasts.

From the hydrodynamic point of view, shear should be taken into consideration, since animal cells are generally shear sensitive. Curran and Black (2005) reported an effective oxygen transport with the increase of Reynolds number, however, they also observed that too high Reynold number may lead to a

decrease of cells in number. This may be resulted from the high fluid shear stress. Santiago *et al.* (2011) suggested that Taylor vortex flow regime is suitable to culture animal cells, where oxygen can be sufficiently provided but with a low fluid shear. Sorg *et al.* (2011) employed a lobed TC reactor to culture cells. They found that compared to the conventional stirred tank reactor, a lower shear stress with a narrower distribution in the TC reactor facilitates cell metabolism. These results remind us to carefully choose an appropriate flow regimes during cell cultivation.

In the light of aforementioned applications, the TC reactor presents many advantages over other chemical reactors. The flow pattern in the TC reactor can be simply and accurately controlled from a laminar flow to a turbulent Taylor vortex flow. While, such unique vortex structure plays an important role in determining particle behaviour. This means that a well control of fluid flow in the TC reactor will be beneficial to obtain desired products. Furthermore, due to its simple configuration, controllable fluid flow, and flexible operation, TC reactor shows a great potential to be applied to a wide range of industrial process.

1.4.3 Computational fluid dynamics in TC reactor

1.4.3.1 Definition of computational fluid dynamics

The use of numerical investigation of the TC reactor to obtain the information of fluid flow is on the rise in recent decades thanks to the rapid development of computer technology. Computational fluid dynamics (CFD) is served as a tool to help the numerical analysis of the fluid flow (Hu, 2012). Rather than obtaining the complicated exact solutions, this technique is powerful and suitable for wide industrial processes (Versteeg and Malalasekera, 2007). As a research and design tool, CFD has several distinct advantages (Anderson and Wendt, 1995; Hu, 2012; and Tu *et al.*, 2018):

- CFD method is economically cheap with reduced time consumption, compared to those experimental-based problems;
- (2) CFD can provide the detailed and comprehensive flow field information, especially for those complicated problems, for which analytical solutions are lacking or wind tunnel testing is difficult to be carried out;
- (3) CFD enables the visualisation of flow field information;
- (4) CFD is flexible, which allows the change of parameters, thereby beneficial to design optimization;
- (5) CFD has the capacity to simulate both realistic and ideal conditions, which are not available in experiment;
- (6) CFD allows the investigation of unwanted situations, such as nuclear power plant failures;
- (7) CFD avoids the contact with harmful or toxic substances.

CFD technique is concerned with the solutions of fluid flow behaviour, such as mass transfer, momentum transfer and heat transfer, also taking the interaction of the fluid with other phases into consideration (Blazek, 2015). The main role of CFD is to solve the engineering problems, which can be converted into mathematical equations by using computer calculation and the specified boundary conditions (Pragati and Sharma, 2012). A complete research system about fluid dynamics, consisting of classical pure experiment, pure theory and the new CFD method is shown in Figure 1.51.



Figure 1.51 Sketch of "three dimensions" in fluid dynamics, reproduced with permission (Anderson and Wendt, 1995, p.7).

1.4.3.2 Governing equations

As all fluid flow behaviour obeys the conservation laws (i.e., mass conservation, momentum conservation and energy conservation), the physical characteristics of the fluid motion can be described by mathematical equations, that is the so-called governing equations (Tu *et al.*, 2018) with a general form of the partial differential equation,

Continuity:

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{u}) = 0 \tag{1.42}$$

x-momentum:

$$\frac{\partial \rho u}{\partial t} + \operatorname{div}(\rho u \boldsymbol{u}) = -\frac{\partial p}{\partial x} + \operatorname{div}(\mu \operatorname{grad} \boldsymbol{u}) + S_u$$
(1.43)

y-momentum:

$$\frac{\partial \rho v}{\partial t} + \operatorname{div}(\rho v \boldsymbol{u}) = -\frac{\partial p}{\partial y} + \operatorname{div}(\mu \operatorname{grad} v) + S_v$$
(1.44)

z-momentum:

$$\frac{\partial \rho w}{\partial t} + \operatorname{div}(\rho w \boldsymbol{u}) = -\frac{\partial p}{\partial z} + \operatorname{div}(\mu \operatorname{grad} w) + S_w$$
(1.45)

Energy:

$$\frac{\partial \rho T}{\partial t} + \operatorname{div}(\rho T \boldsymbol{u}) = \operatorname{div}(\frac{k_T}{c_p} \operatorname{grad} T) + S_T$$
(1.46)

Equation of state:

$$p = p(\rho, T) \tag{1.47}$$

where ρ is the fluid density, u, v, and w are fluid velocities in x, y, and z directions respectively, p is the static pressure, k_T is the thermal conductivity, c_p is the specific heat capacity, and S denotes the source term.

It is obvious that the above equations have a general form,

$$\frac{\partial \rho \Phi}{\partial t} + \operatorname{div}(\rho \Phi \boldsymbol{u}) = \operatorname{div}(\Gamma \operatorname{grad} \Phi) + S_{\Phi}$$
(1.48)

where Φ is a generalized variable, and Γ is the generalized diffusion coefficient. In order to solve the above governing equations, three main numerical methods are often adopted, namely finite-difference method (FDM), finite-element method (FEM), and finite-volume method (FVM). The main features and the differences of these three methods are summarized in Table 1.6. The most commonly used method is FVM due to its high computational efficiency. By employing the numerical method to obtain the solutions for governing equations,

the whole computational domain should firstly be divided into several arbitrary infinitesimal volumes. This process is the so-called discretization. As fluid motion obeys the conservation laws, the net quantity being transported across each arbitrary volume is equal to the flow in minus flow out, shown in Figure 1.52. In Equation (1.48), the first term on the left hand side denotes the rate of change of Φ , and the second term is the flow out due to convection. On the right hand side, the first term is the rate of increase due to diffusion, and the second term is the rate of creation due to sources (Versteeg and Malalasekera, 2007). The key step of FVM is to integrate Equation (1.48) over a three-dimensional infinitesimal volume, as follows,

$$\int_{V} \frac{\partial(\rho\Phi)}{\partial t} dV + \int_{V} \operatorname{div}(\rho\Phi \boldsymbol{u}) dV = \int_{V} \operatorname{div}(\Gamma \operatorname{grad} \Phi) dV + \int_{V} S_{\Phi} dV$$
(1.49)

According to Gauss's divergence theorem, Equation (1.49) can be converted into the integration across a surface limited by boundaries, as follows

$$\frac{\partial}{\partial t} \int_{V} (\rho \Phi) dV + \int_{A} \boldsymbol{n} \cdot (\rho \Phi \boldsymbol{u}) dA = \int_{A} \boldsymbol{n} \cdot (\Gamma \operatorname{grad} \Phi) dA + \int_{V} S_{\Phi} dV \qquad (1.50)$$

Thus, the original governing equations are converted into Equation (1.50). Based on each face boundary, Equation (1.50) is finally written as the algebraic equations, which then can be solved by direct numerical method or iterative method.



Figure 1.52 (a) Finite control volume approach; and (b) Infinitesimal fluid element approach, reproduced with permission (Anderson and Wendt, 1995, p.17).

Method	FDM	FVM	FEM
Principle	Taylor development	Strong form (Stokes formula)	Weak form (Galerkin method)
Geometry	simple	complex	complex
Discretization	regular grid	structured/unstructured	structured/unstructured
Programming	easy	easy for structured	difficult
		difficult for understand	
Matrix	spare	spare	spare
Boundary conditions	to be constructed	to be constructed	naturally constructed

Table 1.6 Comparison of different numerical method, reproduced with permission (Ariyawong, 2015, p.24).

Implementation	rarely implemented in	available in commercial	available in commercial
	commercial software	software especially for:	software especially for:
		-fluid mechanics	-solid mechanics
		-heat transfer	-electromagnetism
		-coupled multiphysics	-heat transfer
			-coupled multiphysics

1.4.3.3 General CFD simulation procedure

In order to perform CFD analysis to solve a specific problem, the procedure can be mainly divided into three steps (Xia and Sun, 2002).

- (1) Pre-processing: Before using CFD method, problems should be described mathematically, that is the set-up of governing equations. Then, initial conditions and boundary conditions are specified based on the actual situation. These conditions, combined with some fluid parameters, as well as physical properties are necessary to obtain the specific solutions of the governing equations. The numerical solution data is located in each infinitesimal volume. That means the geometry should be created, and the computational domain should be determined, followed by meshing. There are many tools for meshing, such as GAMBIT, Hypermesh, and ICEM. After meshing, the computational domain is divided into numerous cells, which enables the next step;
- (2) Processing: Once cells are created, discretized equations is to be solved using software for each cell until the acceptable convergence is achieved. In addition, initial conditions and boundary conditions at this step are converted into the values at each cell node. It often involves numerous discretised equations, which is time consuming and requires a high performance of computer. This process is repeated in an iterative manner until residuals are reduced to specified values;
- (3) Post-processing: As data is available at each cell node, post-processing enables the visualisation of these results through the graphic demonstration of vector, contour, streamline, and trajectory. After

analysis of these data, it can be determined whether the results are in agreement with the actual situation.

The flowchart of the CFD solving procedure is depicted in Figure 1.53.



Figure 1.53 Flowchart of CFD solving procedure.

Today, CFD method has been widely applied in the field of science and engineering. Many commercial software codes are available, such as PHOENICS, the first set of commercial software of CFD and heat transfer; CFX, having a high numerical accuracy due to the use of the FVM based on FEM; STAR-CD, the first commercial software package for fluid flow simulation, and capable of addressing complex geometries; FIDAP, based on FEM; and FLUENT, currently the most widely used one, designed based on CFD "computer software group concept" (Xia and Sun, 2002; Glatzel *et al.*, 2008; and Wei, 2017). The commonly used commercial codes and their websites are listed in Table 1.7 for reference.

CFD code	Company	Web site
CFX	AEA Technology	http://www.software.aeat.com/cfx/
FLUENT	Fluent Inc	http://www.fluent.com/
PHOENICS	Concentration Heat & Momentum Ltd	http://www.cham.co.uk/
	(CHAM)	
STAR-CD	Computational Dynamics Ltd	http://www.cd.co.uk
FLOW3D	Flow Science, Inc	http://www.flow3d.com
CFD-ACE	CFD Research Corporation	http://www.cfdrc.com
ICEM CFD	ICEM Technologies	http://icemcfd.com/icepak.html
AMI-VSAERO	Analytical Methods, Inc (AMI)	http://www.am-inc.com
STORESIM/TETME SH	Computational Mechanics Company, Inc	http://www.comco.com/
IGGTM	NUMECA International SA	http://www.numeca.com/
TECPLOT	Amtec Engineering, Inc	http://www.amtec.com/

Table 1.7 Commercial CFD code list, reproduced with permission (Xia and Sun, 2002, p.11).

PAM-FLOW	Engineering Systems International SA	http://www.esi.com.au/
FLOVENT	Flomerics Inc (FLOVENT)	http://www.flomerics.com/
AVS/EXPRESS	Advanced Visual Systems, Inc	http://www.avs.com/
FLO++	Softflo	http://www.softflo.com/
CFD++	Metacomp Technologies, Inc	http://www.metacomptech.com/

1.5 Recapitulation and concluding remarks

Fine particles generally have significantly different features from atomic clusters or macroscopic substances due to its micro structure and surface effect. Among various preparation methods, reactive precipitation with the advantages of low cost, simple operation and easy to be scaled up has been widely used in industrial application. Crystallisation from aqueous solution is the core step for the generation of stable nuclei. Therefore, this chapter has firstly reviewed the mechanism of particle crystallisation by means of reactive precipitation method. Many steps are involved and co-exist in this process, such as nucleation, crystal growth, agglomeration, breakup, as well as Ostwald ripening. Chemical reactions generally take place in chemical reactors during industrial production, where hydrodynamics plays an important role in affecting final particle properties. On one hand, reactive precipitation generally taking place very fast at a molecular level is induced by a high level of supersaturation, while such supersaturation is created and further redistributed by fluid mixing. On the other hand, hydrodynamic characteristics can influence particle behaviour, such as collision, aggregation, and breakup, and the strong shear induced by turbulent eddies. All these factors lead to the difficulties to interpret the complex interaction between particle formation and hydrodynamic characteristics. However, previous experimental work was mainly conducted in the traditional stirred tank reactor, only focusing on the macro or mean hydrodynamic parameters, such as stirring intensity or power input, but failing to reveal the mechanism of the competition between hydrodynamic mixing and crystallization. Their qualitative observation can only be applicable to their particular reactive precipitation systems. Therefore, mixing theory is necessary for the deep understanding of such mechanism.

A literature review on mixing was secondly presented in this chapter. A brief introduction to macromixing and mesomixing led to a comprehensive understanding of micromixing, as micromixing refers to the mixing at molecular scale. Several widely used micromixing models have been presented. Among these models, the incorporation model will be adopted in this PhD study. Also, experimental methods for evaluating micromixing efficiency have been outlined, where the iodide-iodate method will be presented in Chapter 4. Most of the mixing studies were only conducted by using the chemical probe to evaluate mixing performance, but failing to combine real reactive precipitation system. While for a particle formation system, mixing not only occurs between two liquid streams, but also at liquid-solid interface, where two phase model is more appropriate.

From the literature review, it can be seen see that the experimental investigation of the reactive precipitation process have been widely studied, generally showing qualitative observation. Various mathematical models for theoretical study have been proposed and established, but mostly for single phase flow. Also, few studies combined both the experiment and theoretical model to predict the final particle properties, establish quantitative relationship, and reveal the mechanism of the coupling of between hydrodynamics and particle formation, especially for two-phase flow. As different chemical reactors have different hydrodynamic features, the investigation of coupling mechanism and the establishment of quantitative relationship are very necessary for a wide application. Therefore, current PhD work will take the case of TC reactor as an example for experimental and theoretical studies. The introduction and applications of such reactor, and the fundamentals of CFD simulation were also involved in the literature review. The experimental part of this PhD study will
focus on particle preparation, and CFD modelling will focus on the interaction of flow field and particle motion.

In the following chapters, the investigation of shear controllable synthesis of fine particles using TC reactor is carried out in experiment, assisted by CFD method. This PhD thesis is organized as follows. Chapter 1 gives an elaborate literature review on particle precipitation in chemical reactors. The mechanism of crystallisation is the foundation for particle formation, and this process generally takes place in chemical reactors during industrial production, where hydrodynamics plays an important role in determining final particle properties. Thus, the acknowledgement of crystallisation and deep understanding of the features of various chemical reactors are necessary for the well-controlled preparation of fine particles. Chapter 2 and Chapter 3 will take the case of the preparation of barium sulfate particles as an example to present the relationship of particle properties with the TC reactor features, where Chapter 2 focuses on particle morphology while Chapter 3 concerns particle size. As chemical reaction takes place at the molecular scale, fluid flow behaviour at the micro scale has a direct effect on this course. Thus, an evaluation of the TC reactor performance by micromixing efficiency will be conducted in Chapter 4. For further exploration of the motion of barium sulfate particles under the effect of the typical Taylor vortex, particle tracking simulation will be carried out in Chapter 5. In Chapter 6, the other reaction system will be studied, the synthesis of a cathode material for lithium ion battery, Ni-rich hydroxide particles, which extends the application of the TC reactor. Finally, Chapter 7 will present the main conclusions, derived from previous chapters. Also, based on this PhD work, recommendations for future work will be provided.

References

- Albiter, V., Torres, L.G. and Galindo, E., 1994. Recovery of xanthan from fermentation broths by precipitation in a stirred tank. *Process Biochemistry*, 29(3), pp.187-196.
- Aljishi, M.F., Ruo, A.C., Park, J.H., Nasser, B., Kim, W.S. and Joo, Y.L., 2013. Effect of flow structure at the onset of instability on barium sulfate precipitation in Taylor–Couette crystallizers. *Journal of Crystal Growth*, 373, pp.20-31.
- Andereck, C.D., Liu, S.S. and Swinney, H.L., 1986. Flow regimes in a circular Couette system with independently rotating cylinders. *Journal of Fluid Mechanics*, 164(3), pp.155-183.
- Anderson, J.D. and Wendt, J., 1995. *Computational Fluid Dynamics* (Vol. 206, p. 332). New York: McGraw-Hill.
- Angst, W., Bourne, J.R. and Sharma, R.N., 1982. Mixing and fast chemical reaction—IV The dimensions of the reaction zone. *Chemical Engineering Science*, 37(4), pp.585-590.
- Aoki, N. and Mae, K., 2006. Effects of channel geometry on mixing performance of micromixers using collision of fluid segments. *Chemical Engineering Journal*, 118(3), pp.189-197.
- Aoune, A. and Ramshaw, C., 1999. Process intensification: heat and mass transfer characteristics of liquid films on rotating discs. *International Journal of Heat and Mass Transfer*, *42*(14), pp.2543-2556.
- Appalakutti, S., Sonawane, S., Bhanvase, B.A., Mittal, V. and Ashokkumar, M., 2015. Process intensification of copper chromite (CuCr2O4) nanoparticle production using continuous flow microreactor. *Chemical Engineering and Processing: Process Intensification*, 89, pp.28-34.

- Ariyawong, K., 2015. Process modeling for the growth of SiC using PVT and TSSG methods (Doctoral dissertation, Université Grenoble Alpes, Grenoble).
- Assirelli, M., Bujalski, W., Eaglesham, A. and Nienow, A.W., 2008. Macro-and micromixing studies in an unbaffled vessel agitated by a Rushton turbine. *Chemical Engineering Science*, *63*(1), pp.35-46.
- Aubin, J., Ferrando, M. and Jiricny, V., 2010. Current methods for characterising mixing and flow in microchannels. *Chemical Engineering Science*, 65(6), pp.2065-2093.
- Aubry, C., 1972. Representation des etats de Micromelange resultant de la mise au contract de deux courants d'un fluide homogene. Universite de Nancy I.
- Baber, R., Mazzei, L., Thanh, N.T. and Gavriilidis, A., 2016. Synthesis of silver nanoparticles using a microfluidic impinging jet reactor. *Journal of Flow Chemistry*, 6(3), pp.268-278.
- Baier, G., Graham, M.D. and Lightfoot, E.N., 2000. Mass transport in a novel two-fluid taylor vortex extractor. *AIChE Journal*, *46*(12), pp.2395-2407.
- Baldyga, J. and Bourne, J.R., 1984a. A fluid mechanical approach to turbulent mixing and chemical reaction part I inadequacies of available methods. *Chemical Engineering Communications*, 28(4-6), pp.231-241.
- Baldyga, J. and Bourne, J.R., 1984b. A fluid mechanical approach to turbulent mixing and chemical reaction part II micromixing in the light of turbulence theory. *Chemical Engineering Communications*, 28(4-6), pp.243-258.
- Baldyga, J. and Bourne, J.R., 1984c. A fluid mechanical approach to turbulent mixing and chemical reaction part III computational and experimental results for the new micromixing model. *Chemical Engineering Communications*, 28(4-6), pp.259-281.

- Baldyga, J. and Bourne, J.R., 1989. Simplification of micromixing calculations.I. Derivation and application of new model. *The Chemical Engineering Journal*, 42(2), pp.83-92.
- Baldyga, J. and Bourne, J.R., 1990. Comparison of the engulfment and the interaction-by-exchange-with-the-mean micromixing models. *The Chemical Engineering Journal*, 45(1), pp.25-31.
- Baldyga, J. and Bourne, J.R., 1992. Interactions between mixing on various scales in stirred tank reactors. *Chemical Engineering Science*, 47(8), pp.1839-1848.
- Baldyga, J. and Bourne, J.R., 1999. *Turbulent mixing and chemical reactions*.Wiley.
- Baldyga, J. and Pohorecki, R., 1995. Turbulent micromixing in chemical reactors—a review. *The Chemical Engineering Journal and the Biochemical Engineering Journal*, 58(2), pp.183-195.
- Baldyga, J. and Rohani, S., 1987. Micromixing described in terms of inertialconvective disintegration of large eddies and viscous-convective interactions among small eddies—I. General development and batch systems. *Chemical Engineering Science*, *42*(11), pp.2597-2610.
- Baldyga, J., 1989. Turbulent mixer model with application to homogeneous, instantaneous chemical reactions. *Chemical Engineering Science*, 44(5), pp.1175-1182.
- Baldyga, J., 2016. Mixing and fluid dynamics effects in particle precipitation processes. *KONA Powder and Particle Journal*, *33*, pp.127-149.
- Baldyga, J., Bourne, J.R. and Yang, Y., 1993. Influence of feed pipe diameter on mesomixing in stirred tank reactors. *Chemical Engineering Science*, 48(19), pp.3383-3390.

- Baldyga, J., Bourne, J.R. and Zimmermann, B., 1994. Investigation of mixing in jet reactors using fast, competitive—consecutive reactions. *Chemical Engineering Science*, 49(12), pp.1937-1946.
- Baldyga, J., Podgorska, W. and Pohorecki, R., 1995. Mixing-precipitation model with application to double feed semibatch precipitation. *Chemical Engineering Science*, 50(8), pp.1281-1300.
- Baldyga, J., Rozen, A. and Mostert, F., 1998. A model of laminar micromixing with application to parallel chemical reactions. *Chemical Engineering Journal*, 69(1), pp.7-20.
- Baronas, R., Kulys, J. and Petkevičius, L., 2019. Computational modeling of batch stirred tank reactor based on spherical catalyst particles. *Journal of Mathematical Chemistry*, 57(1), pp.327-342.
- Batchelor, G.K., 1952. The effect of homogeneous turbulence on material lines and surfaces. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 213(1114), pp.349-366.
- Becker, R. and Döring, W., 1935. Kinetische behandlung der keimbildung in übersättigten dämpfen. *Annalen der Physik*, *416*(8), pp.719-752.
- Belevi, H., Bourne, J.R. and Rys, P., 1981. Mixing and fast chemical reaction—
 II: Diffusion-reaction model for the CSTR. *Chemical Engineering Science*, *36*(10), pp.1649-1654.
- Bensaid, S., Deorsola, F.A., Marchisio, D.L., Russo, N. and Fino, D., 2014. Flow field simulation and mixing efficiency assessment of the multi-inlet vortex mixer for molybdenum sulfide nanoparticle precipitation. *Chemical Engineering Journal*, 238, pp.66-77.
- Blazek, J., 2015. Computational fluid dynamics: principles and applications. Butterworth-Heinemann.

- Bodenschatz, E., Pesch, W. and Ahlers, G., 2000. Recent developments in Rayleigh-Bénard convection. *Annual Review of Fluid Mechanics*, 32(1), pp.709-778.
- Boodhoo, K., 2013. Spinning disc reactor for green processing and synthesis. *Process Intensification for Green Chemistry: Engineering Solutions for Sustainable Chemical Processing*, pp.59-90.
- Boodhoo, K.V. and Al-Hengari, S.R., 2012. Micromixing characteristics in a small-scale spinning disk reactor. *Chemical Engineering & Technology*, 35(7), pp.1229-1237.
- Botsaris, G.D., 1976. Industrial Crystallisation. JW Mullin, ed, p.3.
- Boubnov, B.M., Gledzer, E.B. and Hopfinger, E.J., 1995. Stratified circular Couette flow: instability and flow regimes. *Journal of Fluid Mechanics*, 292, pp.333-358.
- Bourne, J. R. and Kozicki, F., 1977. Mixing effects during the bromination of 1,3,5-trimethoxybenzene. *Chemical Engineering Science*, 32(12), pp.1538-1539.
- Bourne, J.R. and Rohani, S., 1983. Micro-mixing and the selective iodination of 1-tyrosine. *Chemical Engineering Research and Design*, *61*(5), pp.297-302.
- Bourne, J.R. and Yu, S., 1994. Investigation of micromixing in stirred tank reactors using parallel reactions. *Industrial & Engineering Chemistry Research*, 33(1), pp.41-55.
- Bourne, J.R., Crivelli, E. and Rys, P., 1977. Chemical selectivities disguised by mass diffusion. V. Mixing-disguised azo coupling reactions. 6th communication on the selectivity of chemical processes. *Helvetica Chimica Acta*, 60(8), pp.2944-2957.

- Bourne, J.R., Kozicki, F. and Rys, P., 1981a. Mixing and fast chemical reaction—I: Test reactions to determine segregation. *Chemical Engineering Science*, 36(10), pp.1643-1648.
- Bourne, J.R., Kozicki, F., Moergeli, U. and Rys, P., 1981b. Mixing and fast chemical reaction—III: Model-experiment comparisons. *Chemical Engineering Science*, 36(10), pp.1655-1663.
- Bourne, J.R., Rys, P. and Suter, K., 1977. Mixing effects in the bromination of resorcin. *Chemical Engineering Science*, *32*(7), pp.711-716.
- Brunsteiner, M., Jones, A.G., Pratola, F., Price, S.L. and Simons, S.J., 2005. Toward a molecular understanding of crystal agglomeration. *Crystal Growth & Design*, 5(1), pp.3-16.
- Bubakova, P., Pivokonsky, M. and Filip, P., 2013. Effect of shear rate on aggregate size and structure in the process of aggregation and at steady state. *Powder Technology*, *235*, pp.540-549.
- Bujalski, W., Nienow, A.W. and Huoxing, L., 1990. The use of upward pumping 45° pitched blade turbine impellers in three-phase reactors. *Chemical Engineering Science*, 45(2), pp.415-421.
- Cafiero, L.M., Baffi, G., Chianese, A. and Jachuck, R.J.J., 2002. Process intensification: precipitation of barium sulfate using a spinning disk reactor. *Industrial & Engineering Chemistry Research*, *41*(21), pp.5240-5246.
- Caimi, S., Cingolani, A., Jaquet, B., Siggel, M., Lattuada, M. and Morbidelli, M., 2017. Tracking of fluorescently labeled polymer particles reveals surface effects during shear-controlled aggregation. *Langmuir*, 33(49), pp.14038-14044.
- Cao, S.B., Han, X.G., Zhang, L.L., Wang, J.X., Luo, Y., Zou, H.K. and Chen, J.F., 2019. Facile and scalable preparation of α -Fe₂O₃ nanoparticle by high-

gravity reactive precipitation method for catalysis of solid propellants combustion. *Powder Technology*, *353*, pp.444-449.

- Carosso, P.A. and Pelizzetti, E., 1984. A stopped-flow technique in fast precipitation kinetics—the case of barium sulphate. *Journal of Crystal Growth*, 68(2), pp.532-536.
- Chella, R. and Ottino, J.M., 1984. Conversion and selectivity modifications due to mixing in unpremixed reactors. *Chemical Engineering Science*, 39(3), pp.551-567.
- Chen, D.L., Gerdts, C.J. and Ismagilov, R.F., 2005. Using microfluidics to observe the effect of mixing on nucleation of protein crystals. *Journal of the American Chemical Society*, *127*(27), pp.9672-9673.
- Chen, J. and Shao, L., 2003. Mass production of nanoparticles by high gravity reactive precipitation technology with low cost. *China Particuology*, *1*(2), pp.64-69.
- Chen, J.F., Shao, L., Guo, F. and Wang, X.M., 2003. Synthesis of nano-fibers of aluminum hydroxide in novel rotating packed bed reactor. *Chemical Engineering Science*, 58(3-6), pp.569-575.
- Chen, J.F., Wang, Y.H., Guo, F., Wang, X.M. and Zheng, C., 2000. Synthesis of nanoparticles with novel technology: high-gravity reactive precipitation. *Industrial & Engineering Chemistry Research*, 39(4), pp.948-954.
- Chen, W. Yue, J. and Yuan, Q., 2008. Gas-liquid microreaction technology: recent developments and future challenges. *Chinese Journal of Chemical Engineering*, 16(5), pp.663-669.
- Cheng, D., Feng, X., Cheng, J., Yang, C. and Mao, Z.S., 2015. Experimental study on the dispersed phase macro-mixing in an immiscible liquid–liquid stirred reactor. *Chemical Engineering Science*, 126, pp.196-203.

- Cheng, D., Feng, X., Yang, C. and Mao, Z.S., 2016. Modelling and experimental investigation of micromixing of single-feed semi-batch precipitation in a liquid–liquid stirred reactor. *Chemical Engineering Journal*, 293, pp.291-301.
- CHENG, J., Xin, F., CHENG, D. and Chao, Y., 2012. Retrospect and perspective of micro-mixing studies in stirred tanks. *Chinese Journal of Chemical Engineering*, 20(1), pp.178-190.
- Chin, S.F., Iyer, K.S., Raston, C.L. and Saunders, M., 2008. Size selective synthesis of superparamagnetic nanoparticles in thin fluids under continuous flow conditions. *Advanced Functional Materials*, 18(6), pp.922-927.
- Chu, G.W., Song, Y.J., Zhang, W.J., Luo, Y., Zou, H.K., Xiang, Y. and Chen, J.F., 2015. Micromixing efficiency enhancement in a rotating packed bed reactor with surface-modified nickel foam packing. *Industrial & Engineering Chemistry Research*, 54(5), pp.1697-1702.
- Costa, P. and Trevissoi, C., 1972. Reactions with non-linear kinetics in partially segregated fluids. *Chemical Engineering Science*, *27*(11), pp.2041-2054.
- Couette, M. M. 1890. Etudes sur le frottement des liquids. Ann. Chim. Phys., 6(Ser.21), pp.433-510.
- Coufort, C., Bouyer, D. and Liné, A., 2005. Flocculation related to local hydrodynamics in a Taylor–Couette reactor and in a jar. *Chemical Engineering Science*, 60(8-9), pp.2179-2192.
- Coughlin, K.T., Marcus, P.S., Tagg, R.P. and Swinney, H.L., 1991. Distinct Quasiperiodic modes with like symmetry in a rotating fluid. *Physical Review Letters*, 66(9), p.1161.

- Crawford, T.C. and Weston, N.P., Pfizer Products Inc and Pfizer Inc, 2003. *Reactive crystallisation method to improve particle size*. U.S. Patent 6,558,435.
- Cristobal, G., Arbouet, L., Sarrazin, F., Talaga, D., Bruneel, J.L., Joanicot, M. and Servant, L., 2006. On-line laser Raman spectroscopic probing of droplets engineered in microfluidic devices. *Lab on a Chip*, 6(9), pp.1140-1146.
- Curl, R.L., 1963. Dispersed phase mixing: I. Theory and effects in simple reactors. *AIChE Journal*, *9*(2), pp.175-181.
- Curran, S.J. and Black, R.A., 2005. Oxygen transport and cell viability in an annular flow bioreactor: Comparison of laminar Couette and Taylor-vortex flow regimes. *Biotechnology and Bioengineering*, 89(7), pp.766-774.
- Danckwerts, P.V., 1953. Continuous flow systems: distribution of residence times. *Chemical Engineering Science*, 2(1), pp.1-13.
- Danckwerts, P.V., 1958. The effect of incomplete mixing on homogeneous reactions. *Chemical Engineering Science*, 8(1-2), pp.93-102.
- Dehkordi, A.M. and Vafaeimanesh, A., 2009. Synthesis of barium sulfate nanoparticles using a spinning disk reactor: effects of supersaturation, disk rotation speed, free ion ratio, and disk diameter. *Industrial & Engineering Chemistry Research*, 48(16), pp.7574-7580.
- DiPrima, R.C. and Swinney, H.L., 1981. Instabilities and transition in flow between concentric rotating cylinders. In *Hydrodynamic Instabilities and the Transition to Turbulence* (pp. 139-180). Springer, Berlin, Heidelberg.
- DiPrima, R.C., Eagles, P.M. and Ng, B.S., 1984. The effect of radius ratio on the stability of Couette flow and Taylor vortex flow. *The Physics of Fluids*, 27(10), pp.2403-2411.

- Dirksen, J.A. and Ring, T.A., 1991. Fundamentals of crystallisation: kinetic effects on particle size distributions and morphology. *Chemical Engineering Science*, *46*(10), pp.2389-2427.
- Dizaji, F.F., Marshall, J.S. and Grant, J.R., 2019. Collision and breakup of fractal particle agglomerates in a shear flow. *Journal of Fluid Mechanics*, 862, pp.592-623.
- Dluska, E., Wroński, S. and Ryszczuk, T., 2004. Interfacial area in gas–liquid Couette–Taylor flow reactor. *Experimental Thermal and Fluid Science*, 28(5), pp.467-472.
- Doku, G.N., Verboom, W., Reinhoudt, D.N. and Van Den Berg, A., 2005. Onmicrochip multiphase chemistry—a review of microreactor design principles and reagent contacting modes. *Tetrahedron*, 61(11), pp.2733-2742.
- Dong, S., 2007. Direct numerical simulation of turbulent Taylor-Couette flow. *Journal of Fluid Mechanics*, 587, p.373.
- Duan, X., Feng, X., Yang, C. and Mao, Z., 2018. CFD modeling of turbulent reacting flow in a semi-batch stirred-tank reactor. *Chinese Journal of Chemical Engineering*, 26(4), pp.675-683.
- Ducoste, J.J., Clark, M.M. and Weetman, R.J., 1997. Turbulence in flocculators: effects of tank size and impeller type. *AIChE Journal*, *43*(2), pp.328-338.
- Durandal, C., Lemenand, T., Della Valle, D. and Peerhossaini, H., 2006, January. A Chemical Probe for Characterising Turbulent Micromixing. In *Fluids Engineering Division Summer Meeting* (Vol. 47500, pp. 1091-1099).
- Dutta, P.K. and Ray, A.K., 2004. Experimental investigation of Taylor vortex photocatalytic reactor for water purification. *Chemical Engineering Science*, *59*(22-23), pp.5249-5259.

- Ehlers, S., Elgeti, K., Menzel, T. and Wießmeier, G., 2000. Mixing in the offstream of a microchannel system. *Chemical Engineering and Processing: Process Intensification*, *39*(4), pp.291-298.
- Ehrfeld, W., Golbig, K., Hessel, V., Löwe, H. and Richter, T., 1999. Characterization of mixing in micromixers by a test reaction: single mixing units and mixer arrays. *Industrial & Engineering Chemistry Research*, 38(3), pp.1075-1082.
- Fan, H.L., Zhou, S.F., Qi, G.S. and Liu, Y.Z., 2016. Continuous preparation of Fe3O4 nanoparticles using impinging stream-rotating packed bed reactor and magnetic property thereof. *Journal of Alloys and Compounds*, 662, pp.497-504.
- Fan, X., Chen, H., Ding, Y., Plucinski, P.K. and Lapkin, A.A., 2008. Potential of 'nanofluids' to further intensify microreactors. *Green Chemistry*, 10(6), pp.670-677.
- Farahani, H.B., Shahrokhi, M. and Dehkordi, A.M., 2017. Experimental investigation and process intensification of barium sulfate nanoparticles synthesis via a new double coaxial spinning disks reactor. *Chemical Engineering and Processing: Process Intensification*, 115, pp.11-22.
- Fenstermacher, P.R., Swinney, H.L. and Gollub, J.P., 1979. Dynamical instabilities and the transition to chaotic Taylor vortex flow. *Journal of Fluid Mechanics*, 94(1), pp.103-128.
- Fournier, M.C., Falk, L. and Villermaux, J., 1996a. A new parallel competing reaction system for assessing micromixing efficiency—determination of micromixing time by a simple mixing model. *Chemical Engineering Science*, 51(23), pp.5187-5192.

- Fournier, M.C., Falk, L. and Villermaux, J., 1996b. A new parallel competing reaction system for assessing micromixing efficiency—experimental approach. *Chemical Engineering Science*, 51(22), pp.5053-5064.
- Garside, J. and Davey, R.J., 1980. Invited review secondary contact nucleation: kinetics, growth and scale-up. *Chemical Engineering Communications*, 4(4-5), pp.393-424.
- Ghanem, A., Lemenand, T., Della Valle, D. and Peerhossaini, H., 2014. Static mixers: Mechanisms, applications, and characterization methods–A review. *Chemical Engineering Research and Design*, 92(2), pp.205-228.
- Glatzel, T., Litterst, C., Cupelli, C., Lindemann, T., Moosmann, C., Niekrawietz, R., Streule, W., Zengerle, R. and Koltay, P., 2008. Computational fluid dynamics (CFD) software tools for microfluidic applications–A case study. *Computers & Fluids*, 37(3), pp.218-235.
- Gorman, M. and Swinney, H.L., 1979. Visual observation of the second characteristic mode in a quasiperiodic flow. *Physical Review Letters*, 43(25), p.1871.
- Gorman, M. and Swinney, H.L., 1982. Spatial and temporal characteristics of modulated waves in the circular Couette system. *Journal of Fluid Mechanics*, 117, pp.123-142.
- Goto, H., Goto, S. and Matsubara, M., 1975. A generalized two-environment model for micromixing in a continuous flow reactor—II. Identification of the model. *Chemical Engineering Science*, *30*(1), pp.71-77.
- Grossmann, S., Lohse, D. and Sun, C., 2016. High–reynolds number taylorcouette turbulence. *Annual Review of Fluid Mechanics*, 48.
- Guichardon, P. and Falk, L., 2000a. Characterisation of micromixing efficiency by the iodide–iodate reaction system. Part I: experimental procedure. *Chemical Engineering Science*, 55(19), pp.4233-4243.

- Guichardon, P., Falk, L. and Villermaux, J., 2000b. Characterisation of micromixing efficiency by the iodide–iodate reaction system. Part II: kinetic study. *Chemical Engineering Science*, 55(19), pp.4245-4253.
- Guo, T.Y., Shi, X., Chu, G.W., Xiang, Y., Wen, L.X. and Chen, J.F., 2016.
 Computational fluid dynamics analysis of the micromixing efficiency in a rotating-packed-bed reactor. *Industrial & Engineering Chemistry Research*, 55(17), pp.4856-4866.
- Haque, J.N., Mahmud, T., Roberts, K.J. and Rhodes, D., 2006. Modeling turbulent flows with free-surface in unbaffled agitated vessels. *Industrial & Engineering Chemistry Research*, 45(8), pp.2881-2891.
- Haut, B., Amor, H.B., Coulon, L., Jacquet, A. and Halloin, V., 2003.
 Hydrodynamics and mass transfer in a Couette–Taylor bioreactor for the culture of animal cells. *Chemical Engineering Science*, 58(3-6), pp.777-784.
- Hessel, V., Hardt, S., Löwe, H. and Schönfeld, F., 2003. Laminar mixing in different interdigital micromixers: I. Experimental characterization. *AIChE Journal*, 49(3), pp.566-577.
- Hetherington, P., Scalley, M.J. and Jachuck, R.J.J., 2001, September. Process intensification: continuous production of barium sulphate using a spinning cone precipitator. In 4th International Conference on Process Intensification for the Chemical Industry.
- Hoffmann, M., Schlüter, M. and Räbiger, N., 2006. Experimental investigation of liquid–liquid mixing in T-shaped micro-mixers using μ-LIF and μ-PIV. *Chemical Engineering Science*, 61(9), pp.2968-2976.
- Hu, H.H., 2012. Computational fluid dynamics. In *Fluid Mechanics* (pp. 421-472). Academic Press.

- Hua, W., Wu, Z., Chen, M., Knapp, M., Guo, X., Indris, S., Binder, J.R., Bramnik, N.N., Zhong, B., Guo, H. and Chou, S., 2017. Shape-controlled synthesis of hierarchically layered lithium transition-metal oxide cathode materials by shear exfoliation in continuous stirred-tank reactors. *Journal* of Materials Chemistry A, 5(48), pp.25391-25400.
- Huisman, S.G., Van Der Veen, R.C., Sun, C. and Lohse, D., 2014. Multiple states in highly turbulent Taylor–Couette flow. *Nature Communications*, 5(1), pp.1-5.
- Jacobsen, N.C. and Hinrichsen, O., 2012. Micromixing efficiency of a spinning disk reactor. *Industrial & Engineering Chemistry Research*, 51(36), pp.11643-11652.
- Jagannathan, R., Sung, C.Y., Youngquist, G.R. and Estrin, J., 1980, January. Fluid Secondary Nucleation of Magnesium Sulfate and Potassium Aluminium Sulfate. In *AIChE Symposium Series* (Vol. 76, No. 193, pp. 90-97). American Institute of Chemical Engineers.
- Jahanshahi-Anboohi, J. and Molaei Dehkordi, A., 2019. Continuous synthesis of barium sulfate nanoparticles in a new high-speed spinning disk reactor. *Industrial & Engineering Chemistry Research*, 58(36), pp.16597-16609.
- Jaworski, Z., Bujalski, W., Otomo, N. and Nienow, A.W., 2000. CFD study of homogenization with dual Rushton turbines—comparison with experimental results: part I: initial studies. *Chemical Engineering Research* and Design, 78(3), pp.327-333.
- Jiang, M., Li, Y.E.D., Tung, H.H. and Braatz, R.D., 2015. Effect of jet velocity on crystal size distribution from antisolvent and cooling crystallisations in a dual impinging jet mixer. *Chemical Engineering and Processing: Process Intensification*, 97, pp.242-247.

- Johnson, B.K. and Prud'homme, R.K., 2003. Chemical processing and micromixing in confined impinging jets. *AIChE Journal*, 49(9), pp.2264-2282.
- Johnson, B.K., 2004. Flash NanoPrecipitation of organic actives via confined micromixing and block copolymer stabilization (Doctoral dissertation, Princeton University, Princeton).
- Johnson, T.J., Ross, D. and Locascio, L.E., 2002. Rapid microfluidic mixing. *Analytical Chemistry*, 74(1), pp.45-51.
- Jung, W.M., Kang, S.H., Kim, K.S., Kim, W.S. and Choi, C.K., 2010. Precipitation of calcium carbonate particles by gas–liquid reaction: Morphology and size distribution of particles in Couette-Taylor and stirred tank reactors. *Journal of Crystal Growth*, 312(22), pp.3331-3339.
- Jung, W.M., Kang, S.H., Kim, W.S. and Choi, C.K., 2000. Particle morphology of calcium carbonate precipitated by gas–liquid reaction in a Couette– Taylor reactor. *Chemical Engineering Science*, 55(4), pp.733-747.
- Justen, P., Paul, G.C., Nienow, A.W. and Thomas, C.R., 1998. Dependence of Penicillium chrysogenum growth, morphology, vacuolation, and productivity in fed-batch fermentations on impeller type and agitation intensity. *Biotechnology and Bioengineering*, 59(6), pp.762-775.
- Kang, S.H., Lee, S.G., Jung, W.M., Kim, M.C., Kim, W.S., Choi, C.K. and Feigelson, R.S., 2003. Effect of Taylor vortices on calcium carbonate crystallisation by gas–liquid reaction. *Journal of Crystal Growth*, 254(1-2), pp.196-205.
- Kasat, G.R., Khopkar, A.R., Ranade, V.V. and Pandit, A.B., 2008. CFD simulation of liquid-phase mixing in solid–liquid stirred reactor. *Chemical Engineering Science*, 63(15), pp.3877-3885.

- Keairns, D.L. and Manning, F.S., 1969. Model simulation of adiabatic continuous flow stirred tank reactors. *AIChE Journal*, *15*(5), pp.660-665.
- Keeler, R.N., Petersen, E.E. and Prausnitz, J.M., 1965. Mixing and chemical reaction in turbulent flow reactors. *AIChE Journal*, *11*(2), pp.221-227.
- Keoschkerjan, R., Richter, M., Boskovic, D., Schnürer, F. and Löbbecke, S., 2004. Novel multifunctional microreaction unit for chemical engineering. *Chemical Engineering Journal*, 101(1-3), pp.469-475.
- Khan, W.H. and Rathod, V.K., 2014. Process intensification approach for preparation of curcumin nanoparticles via solvent–nonsolvent nanoprecipitation using spinning disc reactor. *Chemical Engineering and Processing: Process Intensification*, 80, pp.1-10.
- Kim, J.E. and Kim, W.S., 2017. Synthesis of Core–Shell Particles of Nickel– Manganese–Cobalt Hydroxides in a Continuous Couette-Taylor Crystallizer. *Crystal Growth & Design*, 17(7), pp.3677-3686.
- Kim, J.M., Chang, S.M., Chang, J.H. and Kim, W.S., 2011. Agglomeration of nickel/cobalt/manganese hydroxide crystals in Couette–Taylor crystallizer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384(1-3), pp.31-39.
- Kim, J.S., Kim, D.H., Gu, B. and Yang, D.R., 2013. Simulation of Taylor– Couette reactor for particle classification using CFD. *Journal of Crystal Growth*, 373, pp.106-110.
- Kim, W.S., 2014. Application of Taylor vortex to crystallisation. *Journal of Chemical Engineering of Japan*, 47(2), pp.115-123.
- Klein, J.P., David, R. and Villermaux, J., 1980. Interpretation of experimental liquid phase micromixing phenomena in a continuous stirred reactor with short residence times. *Industrial & Engineering Chemistry Fundamentals*, 19(4), pp.373-379.

- Knight, J.B., Vishwanath, A., Brody, J.P. and Austin, R.H., 1998.
 Hydrodynamic focusing on a silicon chip: mixing nanoliters in microseconds. *Physical Review Letters*, 80(17), p.3863.
- Kockmann, N., Kiefer, T., Engler, M. and Woias, P., 2006. Silicon microstructures for high throughput mixing devices. *Microfluidics and Nanofluidics*, 2(4), pp.327-335.
- Kong, L.N., Li, W., Han, L.C., Liu, Y.J., Luo, H.A., Al Dahhan, M. and Dudukovic, M.P., 2012. On the measurement of gas holdup distribution near the region of impeller in a gas–liquid stirred Rushton tank by means of γ-CT. *Chemical Engineering Journal*, *188*, pp.191-198.
- Krishnaraj, K.P. and Nott, P.R., 2016. A dilation-driven vortex flow in sheared granular materials explains a rheometric anomaly. *Nature Communications*, 7, p.10630.
- Kugler, R.T. and Kind, M., 2016. Experimental study about plugging in confined impinging jet mixers during the precipitation of strontium sulfate. *Chemical Engineering and Processing: Process Intensification*, 101, pp.25-32.
- Kukukova, A., Aubin, J. and Kresta, S.M., 2009. A new definition of mixing and segregation: three dimensions of a key process variable. *Chemical Engineering Research and Design*, 87(4), pp.633-647.
- LaRosa, P. and Manning, F.S., 1964. Intensity of segregation as a measure of incomplete mixing. *The Canadian Journal of Chemical Engineering*, 42(2), pp.65-68.
- Lathrop, D.P., Fineberg, J. and Swinney, H.L., 1992. Turbulent flow between concentric rotating cylinders at large Reynolds number. *Physical Review Letters*, 68(10), p.1515.

- Lee, S.W., Kim, D.S., Lee, S.S. and Kwon, T.H., 2006. A split and recombination micromixer fabricated in a PDMS three-dimensional structure. *Journal of Micromechanics and Microengineering*, 16(5), p.1067.
- Lehwald, A., Janiga, G., Thévenin, D. and Zähringer, K., 2012. Simultaneous investigation of macro-and micro-mixing in a static mixer. *Chemical Engineering Science*, 79, pp.8-18.
- Lemenand, T., Della Valle, D., Habchi, C. and Peerhossaini, H., 2017. Micromixing measurement by chemical probe in homogeneous and isotropic turbulence. *Chemical Engineering Journal*, 314, pp.453-465.
- Li, G., Yang, X. and Ye, H., 2015. CFD simulation of shear flow and mixing in a Taylor–Couette reactor with variable cross-section inner cylinders. *Powder Technology*, 280, pp.53-66.
- Li, W., Xia, F., Qin, H., Zhang, M., Li, W. and Zhang, J., 2019. Numerical and experimental investigations of micromixing performance and efficiency in a pore-array intensified tube-in-tube microchannel reactor. *Chemical Engineering Journal*, 370, pp.1350-1365.
- Lin, C.C., Lin, Y.S. and Ho, J.M., 2016. Adsorption of Reactive Red 2 from aqueous solutions using Fe₃O₄ nanoparticles prepared by co-precipitation in a rotating packed bed. *Journal of Alloys and Compounds*, 666, pp.153-158.
- Lindrud, M.D., Kim, S. and Wei, C., Bristol Myers Squibb Co, 2001. Sonic impinging jet crystallisation apparatus and process. U.S. Patent 6,302,958.
- Liu, D., Wang, Z., Chen, X. and Liu, M., 2018. Simulation of agglomerate breakage and restructuring in shear flows: Coupled effects of shear gradient, surface energy and initial structure. *Powder Technology*, 336, pp.102-111.

- Liu, L., Yang, X., Li, G., Huang, X. and Xue, C., 2020. Shear controllable synthesis of barium sulfate particles using lobed inner cylinder Taylor-Couette flow reactor. *Advanced Powder Technology*, *31*(3), pp.1088-1099.
- Lu, W.M., Wu, H.Z. and Ju, M.Y., 1997. Effects of baffle design on the liquid mixing in an aerated stirred tank with standard Rushton turbine impellers. *Chemical Engineering Science*, *52*(21-22), pp.3843-3851.
- Luo, J.Z., Luo, Y., Chu, G.W., Arowo, M., Xiang, Y., Sun, B.C. and Chen, J.F., 2016. Micromixing efficiency of a novel helical tube reactor: CFD prediction and experimental characterization. *Chemical Engineering Science*, 155, pp.386-396.
- Mahajan, A.J. and Kirwan, D.J., 1994. Nucleation and growth kinetics of biochemicals measured at high supersaturations. *Journal of Crystal Growth*, 144(3-4), pp.281-290.
- Mahajan, A.J. and Kirwan, D.J., 1996. Micromixing effects in a two-impingingjets precipitator. *AIChE Journal*, 42(7), pp.1801-1814.
- Makataka, S. and Kobayashi, J., 1976. Micromixing model and experimental study in a continuous stirred-tank reactor. *International Chemical Engineering*, *16*(1), pp.148-154.
- Manzano Martínez, A.N., van Eeten, K.M., Schouten, J.C. and van der Schaaf, J., 2017. Micromixing in a rotor–stator spinning disc reactor. *Industrial & Engineering Chemistry Research*, 56(45), pp.13454-13460.
- Mao, K.W. and Toor, H.L., 1970. A diffusion model for reactions with turbulent mixing. *AIChE Journal*, *16*(1), pp.49-52.
- Mao, K.W. and Toor, H.L., 1971. Second-order chemical reactions with turbulent mixing. *Industrial & Engineering Chemistry Fundamentals*, 10(2), pp.92-197.

- Mao, Z. and Yang, C., 2017. Micro-mixing in chemical reactors: a perspective. *Chinese Journal of Chemical Engineering*, 25(4), pp.381-390.
- Marchisio, D.L., Omegna, F. and Barresi, A.A., 2009. Production of TiO2 nanoparticles with controlled characteristics by means of a Vortex Reactor. *Chemical Engineering Journal*, 146(3), pp.456-465.
- Marchisio, D.L., Rivautella, L. and Barresi, A.A., 2006. Design and scale-up of chemical reactors for nanoparticle precipitation. *AIChE Journal*, 52(5), pp.1877-1887.
- Masca, S.I., Rodriguez-Mendieta, I.R., Friel, C.T., Radford, S.E. and Smith, D.A., 2006. Detailed evaluation of the performance of microfluidic T mixers using fluorescence and ultraviolet resonance Raman spectroscopy. *Review of Scientific Instruments*, 77(5), p.055105.
- Mavros, P., 2001. Flow visualisation in stirred vessels: A review of experimental techniques. *Chemical Engineering Research and Design*, 79(2), pp.113-127.
- Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-Rich hydroxide in reaction crystallisation: Effect of Taylor vortex dimension and intensity. *Crystal Growth & Design*, *15*(4), pp.1726-1734.
- Mehta, R.V. and Tarbell, J.M., 1983a. Four environment model of mixing and chemical reaction. Part I. Model development. *AIChE Journal*, 29(2), pp.320-329.
- Mehta, R.V. and Tarbell, J.M., 1983b. Four environment model of mixing and chemical reaction. Part II. Comparison with experiments. *AIChE Journal*, 29(2), pp.329-337.

Mersmann, A. ed., 2001. Crystallisation technology handbook. CRC press.

- Methot, J. C. and Roy, P. H., 1973. Experimental evaluation of a model-based degree of segregation in a CSTR. *Chemical Engineering Science*, 28, pp.1961-1966.
- Midler Jr, M., Paul, E.L., Whittington, E.F., Futran, M., Liu, P.D., Hsu, J. and Pan, S.H., Merck and Co Inc, 1994. *Crystallisation method to improve crystal structure and size*. U.S. Patent 5,314,506.
- Miyairi, Y., Kamiwano, M. and Yamamoto, K., 1971. Turbulent mixing in a tubular flow reactor. *International Chemical Engineering*, 11(2), p.344.
- MIYAWAKI, O., TSUJIKAWA, H. and URAGUCHI, Y., 1975. Chemical reactions under incomplete mixing. *Journal of Chemical Engineering of Japan*, 8(1), pp.63-68.
- Mohammadi, S., Harvey, A. and Boodhoo, K.V., 2014. Synthesis of TiO2 nanoparticles in a spinning disc reactor. *Chemical Engineering Journal*, 258, pp.171-184.
- Mullin, J.W., 2000. Crystallisation and precipitation. *Ullmann's Encyclopedia* of Industrial Chemistry.
- Myerson, A., 2002. Handbook of industrial crystallisation. Butterworth-Heinemann.
- Nabholz, F. and Rys, P., 1977. Chemical selectivities disguised by mass diffusion. IV. Mixing-disguised nitrations of aromatic compounds with nitronium salts. 4th communication on the selectivity of chemical processes. *Helvetica Chimica Acta*, 60(8), pp.2937-2943.
- Nagasawa, H., Aoki, N. and Mae, K., 2005. Design of a new micromixer for instant mixing based on the collision of micro segments. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 28(3), pp.324-330.

- Nauman, E.B., 1975. The droplet diffusion model for micromixing. *Chemical Engineering Science*, *30*(9), pp.1135-1140.
- Nguyen, A.T., Joo, Y.L. and Kim, W.S., 2012. Multiple feeding strategy for phase transformation of GMP in continuous Couette–Taylor crystallizer. *Crystal Growth & Design*, *12*(6), pp.2780-2788.
- Nguyen, A.T., Kim, J.M., Chang, S.M. and Kim, W.S., 2010. Taylor vortex effect on phase transformation of guanosine 5-monophosphate in drowning-out crystallisation. *Industrial & Engineering Chemistry Research*, 49(10), pp.4865-4872.
- Nguyen, A.T., Kim, J.M., Chang, S.M. and Kim, W.S., 2011. Phase Transformation of Guanosine 5-Monophosphate in Continuous Couette– Taylor Crystallizer: Experiments and Numerical Modeling for Kinetics. *Industrial & Engineering Chemistry Research*, 50(6), pp.3483-3493.
- Nguyen, A.T., Yu, T. and Kim, W.S., 2017. Couette-Taylor crystallizer: Effective control of crystal size distribution and recovery of L-lysine in cooling crystallisation. *Journal of Crystal Growth*, 469, pp.65-77.

Nielsen, A.E., 1964. Kinetics of precipitation (Vol. 18). Pergamon.

- Nienow, A.W., 1996. Gas-Liquid Mixing Studies-A Comparison of Rushton Turbines with Some Modern Impellers. *Chemical Engineering Research & Design*, 74(4), pp.417-423.
- Niu, L., Chu, Z., Cai, M. and Liu, M., 2019. Modified Force Balance Model of Estimating Agglomerate Sizes in a Gas–Solid Fluidized Bed. *Industrial & Engineering Chemistry Research*, 58(19), pp.8472-8483.

Nývlt, J., 1971. Industrial crystallisation from solutions. Butterworths.

- Ohmura, N., Suemasu, T. and Asamura, Y., 2005, January. Particle classification in Taylor vortex flow with an axial flow. In *Journal of Physics: Conference Series*, *14*, pp. 64-71.
- Ojaniemi, U., Puranen, J., Manninen, M., Gorshkova, E. and Louhi-Kultanen, M., 2018. Hydrodynamics and kinetics in semi-batch stirred tank precipitation of l-glutamic acid based on pH shift with mineral acids. *Chemical Engineering Science*, 178, pp.167-182.
- Ott, R.J. and Rys, P., 1975. Chemical Selectivities Disguised by Mass Diffusion I. A simple model of mixing-disguised reactions in solution. 1st communication on the selectivity of chemical processes. *Helvetica Chimica Acta*, 58(7), pp.2074-2093.
- Ottino, J.M., 1980. Lamellar mixing models for structured chemical reactions and their relationship to statistical models; Macro-and micromixing and the problem of averages. *Chemical Engineering Science*, *35*(6), pp.1377-1381.
- Ottino, J.M., 1981. Efficiency of mixing from data on fast reactions in multi-jet reactors and stirred tanks. *AIChE Journal*, 27(2), pp.184-192.
- Ottino, J.M., 1982. Description of mixing with diffusion and reaction in terms of the concept of material surfaces. *Journal of Fluid Mechanics*, *114*, pp.83-103.
- Ottino, J.M., Ranz, W.E. and Macosko, C.W., 1979. A lamellar model for analysis of liquid-liquid mixing. *Chemical Engineering Science*, 34(6), pp.877-890.
- Ouyang, Y., Xiang, Y., Gao, X.Y., Li, W.L., Zou, H.K., Chu, G.W. and Chen, J.F., 2018. Micromixing efficiency in a rotating packed bed with non-Newtonian fluid. *Chemical Engineering Journal*, 354, pp.162-171.
- Oxley, P., Brechtelsbauer, C., Ricard, F., Lewis, N. and Ramshaw, C., 2000. Evaluation of spinning disk reactor technology for the manufacture of

pharmaceuticals. *Industrial & Engineering Chemistry Research*, 39(7), pp.2175-2182.

- Panić, S., Loebbecke, S., Tuercke, T., Antes, J. and Bošković, D., 2004. Experimental approaches to a better understanding of mixing performance of microfluidic devices. *Chemical Engineering Journal*, 101(1-3), pp.409-419.
- Paul, E.L. and Treybal, R.E., 1971. Mixing and product distribution for a liquidphase, second-order, competitive-consecutive reaction. *AIChE Journal*, 17(3), pp.718-724.
- Paul, E.L., Mahadevan, H., Foster, J., Kennedy, M. and Midler, M., 1992. The effect of mixing on scaleup of a parallel reaction system. *Chemical Engineering Science*, 47(9-11), pp.2837-2840.
- Paul, E.L., Tung, H.H. and Midler, M., 2005. Organic crystallisation processes. *Powder Technology*, 150(2), pp.133-143.
- Phelan, K.G. and Stedman, G., 1981. Nitrogen tracer evidence for a cyclic azide species. *Journal of the Chemical Society, Chemical Communications*, (6), pp.299-300.
- Pohorecki, R. and Baldyga, J., 1983. New model of micromixing in chemical reactors. 1. General development and application to a tubular reactor. *Industrial & Engineering Chemistry Fundamentals*, 22(4), pp.392-397.
- Pohorecki, R. and Baldyga, J., 1985. The effect of micromixing on the precipitation process in a premixed feed continuous stirred tank crystallizer (CSTC). In *Proceedings of 5th Conference on Mixing*.
- Powers, H.E.C., 1963. Nucleation and early crystal growth. *Ind. Chem.*, 39, pp.351-355.

- Pragati, K. and Sharma, H.K., 2012. Concept of computational fluid dynamics (CFD) and its applications in food processing equipment design. *Journal of Food Processing and Technology*, 3(1).
- Prat, O.P. and Ducoste, J.J., 2006. Modeling spatial distribution of floc size in turbulent processes using the quadrature method of moment and computational fluid dynamics. *Chemical Engineering Science*, *61*(1), pp.75-86.
- Qiao, J., Deng, R. and Wang, C.H., 2015. Particle motion in a Taylor vortex. *International Journal of Multiphase Flow*, 77, pp.120-130.
- Qin, H., Zhang, C., Xu, Q., Dang, X., Li, W., Lei, K., Zhou, L. and Zhang, J., 2017. Geometrical improvement of inline high shear mixers to intensify micromixing performance. *Chemical Engineering Journal*, 319, pp.307-320.
- Raghav Rao, K.S.M.S. and Joshi, J.B., 1988. Liquid phase mixing in mechanically agitated vessels. *Chemical Engineering Communications*, 74(1), pp.1-25.
- Ramshaw, C., 1995. The incentive for process intensification. In *BHR Group Conference Series Publication* (Vol. 18, pp. 1-4). Mechanical Engineering Publications Limited.
- Ranade, V.V. and Joshi, J.B., 1990. Flow generated by a disc turbine. II: Mathematical modelling and comparison with experimental data. *Chemical Engineering Research & Design*, 68(1), pp.34-50.
- Ranz, W.E., 1979. Applications of a stretch model to mixing, diffusion, and reaction in laminar and turbulent flows. *AIChE Journal*, *25*(1), pp.41-47.
- Rao, D.P., Bhowal, A. and Goswami, P.S., 2004. Process intensification in rotating packed beds (HIGEE): an appraisal. *Industrial & Engineering Chemistry Research*, 43(4), pp.1150-1162.

- Richter, O., Hoffmann, H. and Kraushaar-Czarnetzki, B., 2008. Effect of the rotor shape on the mixing characteristics of a continuous flow Taylor-vortex reactor. *Chemical Engineering Science*, *63*(13), pp.3504-3513.
- Richter, O., Menges, M. and Kraushaar-Czarnetzki, B., 2009. Investigation of mixing in a rotor shape modified Taylor-vortex reactor by the means of a chemical test reaction. *Chemical Engineering Science*, 64(10), pp.2384-2391.
- Ritchie, B.W. and Tobgy, A.H., 1979. A three-environment micromixing model for chemical reactors with arbitrary separate feedstreams. *The Chemical Engineering Journal*, 17(3), pp.173-182.
- Salmon, J.B., Ajdari, A., Tabeling, P., Servant, L., Talaga, D. and Joanicot, M., 2005. In situ Raman imaging of interdiffusion in a microchannel. *Applied physics letters*, 86(9), p.094106.
- Sanchez, A., Martinez, A., Torres, L. and Galindo, E., 1992. Power consumption of three impeller combinations in mixing xanthan fermentation broths. *Process Biochemistry*, 27(6), pp.351-365.
- Santiago, P.A., de Campos Giordano, R. and Suazo, C.A.T., 2011. Performance of a vortex flow bioreactor for cultivation of CHO-K1 cells on microcarriers. *Process Biochemistry*, 46(1), pp.35-45.
- Santillo, G., Deorsola, F.A., Bensaid, S., Russo, N. and Fino, D., 2012. MoS2 nanoparticle precipitation in turbulent micromixers. *Chemical Engineering Journal*, 207, pp.322-328.
- Schaer, E., Guichardon, P., Falk, L. and Plasari, E., 1999. Determination of local energy dissipation rates in impinging jets by a chemical reaction method. *Chemical Engineering Journal*, 72(2), pp.125-138.
- Schnebelen, M., Mozet, K., Jakob, A., Sy, D., Plasari, E. and Muhr, H., 2015. Agglomeration Mechanisms and Kinetics during the Carbonation of a

Suspension of Lime in a Pilot Batch Reactor. *Crystal Structure Theory and Applications*, 4(03), p.35.

- Schonfeld, F., Hessel, V. and Hofmann, C., 2004. An optimised split-andrecombine micro-mixer with uniform 'chaotic'mixing. *Lab on a Chip*, *4*(1), pp.65-69.
- Schwarzer, H.C. and Peukert, W., 2002. Experimental investigation into the influence of mixing on nanoparticle precipitation. *Chemical Engineering & Technology*, 25(6), pp.657-661.
- Selomulya, C., Amal, R., Bushell, G. and Waite, T.D., 2001. Evidence of shear rate dependence on restructuring and breakup of latex aggregates. *Journal of Colloid and Interface Science*, 236(1), pp.67-77.
- Selomulya, C., Bushell, G., Amal, R. and Waite, T.D., 2002. Aggregation mechanisms of latex of different particle sizes in a controlled shear environment. *Langmuir*, 18(6), pp.1974-1984.
- Serra, T., Colomer, J. and Casamitjana, X., 1997. Aggregation and breakup of particles in a shear flow. *Journal of Colloid and Interface Science*, 187(2), pp.466-473.
- Shaddel, S., Ucar, S., Andreassen, J.P. and Østerhus, S.W., 2019. Engineering of struvite crystals by regulating supersaturation–correlation with phosphorus recovery, crystal morphology and process efficiency. *Journal of Environmental Chemical Engineering*, 7(1), p.102918.
- Sharp, K.V. and Adrian, R.J., 2001. PIV study of small-scale flow structure around a Rushton turbine. *AIChE Journal*, 47(4), pp.766-778.
- Shaw, R.S., Andereck, C.D., Reith, L.A. and Swinney, H.L., 1982. Superposition of traveling waves in the circular Couette system. *Physical Review Letters*, 48(17), p.1172.

- Siddiqui, S.W., Zhao, Y., Kukukova, A. and Kresta, S.M., 2009a. Characteristics of a confined impinging jet reactor: energy dissipation, homogeneous and heterogeneous reaction products, and effect of unequal flow. *Industrial & Engineering Chemistry Research*, 48(17), pp.7945-7958.
- Siddiqui, S.W., Unwin, P.J., Xu, Z. and Kresta, S.M., 2009b. The effect of stabilizer addition and sonication on nanoparticle agglomeration in a confined impinging jet reactor. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 350(1-3), pp.38-50.
- Smith, M. and Matsoukas, T., 1998. Constant-number Monte Carlo simulation of population balances. *Chemical Engineering Science*, 53(9), pp.1777-1786.
- Sobczak, E., 1990. A simple method of determination of mass transfer coefficients and surface reaction constants for crystals growth. *Chemical Engineering Science*, *45*(2), pp.561-564.
- Söhnel, O. and Garside, J., 1992. *Precipitation: basic principles and industrial applications*. Butterworth-Heinemann.
- Soos, M., Wu, H. and Morbidelli, M., 2007. Taylor-Couette unit with a lobed inner cylinder cross section. *AIChE Journal*, *53*(5), pp.1109-1120.
- Sorg, R., Tanzeglock, T., Soos, M., Morbidelli, M., Périlleux, A., Solacroup, T. and Broly, H., 2011. Minimizing hydrodynamic stress in mammalian cell culture through the lobed Taylor-Couette bioreactor. *Biotechnology Journal*, 6(12), pp.1504-1515.
- Spicer, P.T. and Pratsinis, S.E., 1996. Shear-induced flocculation: the evolution of floc structure and the shape of the size distribution at steady state. *Water Research*, 30(5), pp.1049-1056.

- Spicer, P.T., Keller, W. and Pratsinis, S.E., 1996. The effect of impeller type on floc size and structure during shear-induced flocculation. *Journal of Colloid and Interface Science*, *184*(1), pp.112-122.
- Spielman, L.A. and Levenspiel, O., 1965. A Monte Carlo treatment for reacting and coalescing dispersed phase systems. *Chemical Engineering Science*, 20(3), pp.247-254.
- Stahl, M., Aslund, B.L. and Rasmuson, A.C., 2001. Reaction crystallisation kinetics of benzoic acid. AIChE Journal, 47(7), pp.1544-1560.
- Stankiewicz, A.I. and Moulijn, J.A., 2000. Process intensification: transforming chemical engineering. *Chemical Engineering Progress*, *96*(1), pp.22-34.
- Stroock, A.D., Dertinger, S.K., Ajdari, A., Mezić, I., Stone, H.A. and Whitesides, G.M., 2002. Chaotic mixer for microchannels. *Science*, 295(5555), pp.647-651.
- Sudarsan, A.P. and Ugaz, V.M., 2006. Multivortex micromixing. *Proceedings* of the National Academy of Sciences, 103(19), pp.7228-7233.
- Sung, C.Y., Estrin, J. and Youngquist, G.R., 1973. Secondary nucleation of magnesium sulfate by fluid shear. *AIChE Journal*, *19*(5), pp.957-962.
- Swift, J.B., Gorman, M. and Swinney, H.L., 1982. Modulated wavy vortex flow in laboratory and rotating reference frames. *Physics Letters A*, 87(9), pp.457-460.
- Taghavi, M. and Moghaddas, J., 2019. Using PLIF/PIV techniques to investigate the reactive mixing in stirred tank reactors with Rushton and pitched blade turbines. *Chemical Engineering Research and Design*, 151, pp.190-206.
- Taghavi, M., Zadghaffari, R., Moghaddas, J. and Moghaddas, Y., 2011. Experimental and CFD investigation of power consumption in a dual

Rushton turbine stirred tank. *Chemical Engineering Research and Design*, 89(3), pp.280-290.

- Tai, C.Y., Tai, C.T., Chang, M.H. and Liu, H.S., 2007. Synthesis of magnesium hydroxide and oxide nanoparticles using a spinning disk reactor. *Industrial & Engineering Chemistry Research*, 46(17), pp.5536-5541.
- Takebayashi, Y., Sue, K., Yoda, S., Furuya, T. and Mae, K., 2012. Direct carbonylation of nitrobenzene to phenylisocyanate using gas–liquid slug flow in microchannel. *Chemical Engineering Journal*, 180, pp.250-254.
- Tamir, A., 2014. Impinging-stream reactors: fundamentals and applications (Vol. 7). Elsevier.
- Tanzeglock, T., 2008. A novel lobed Taylor-Couette bioreactor for the cultivation of shear sensitive cells and tissues (Doctoral dissertation, ETH, Zurich).
- Taylor, G.I., 1923. VIII. Stability of a viscous liquid contained between two rotating cylinders. *Philosophical Transactions of the Royal Society of London. Series A, Containing Papers of a Mathematical or Physical Character*, 223(605-615), pp.289-343.
- Taylor, G.I., 1936. Fluid friction between rotating cylinders I—Torque measurements. Proceedings of the Royal Society of London. Series A-Mathematical and Physical Sciences, 157(892), pp.546-564.
- Thai, D.K., Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-rich hydroxide crystals in Taylor vortex flow. *Powder Technology*, 274, pp.5-13.
- Torbacke, M. and Rasmuson, Å.C., 2004. Mesomixing in semi-batch reaction crystallisation and influence of reactor size. *AIChE Journal*, 50(12), pp.3107-3119.

- Torrest, R.S. and Ranz, W.E., 1969. Improved conductivity system for measurement of turbulent concentration fluctuations. *Industrial & Engineering Chemistry Fundamentals*, 8(4), pp.810-816.
- Trad, Z., Fontaine, J.P., Larroche, C. and Vial, C., 2017. Experimental and numerical investigation of hydrodynamics and mixing in a dual-impeller mechanically-stirred digester. *Chemical Engineering Journal*, 329, pp.142-155.
- Treleaven, C.R. and Tobgy, A.H., 1973. Residence times, micromixing and conversion in an un-premixed feed reactor—II: Chemical reaction measurements. *Chemical Engineering Science*, 28(2), pp.413-425.
- Trippa, G. and Jachuck, R.J.J., 2003. Process intensification: precipitation of calcium carbonate using narrow channel reactors. *Chemical Engineering Research and Design*, 81(7), pp.766-772.
- Truong, K.T. and Methot, J.C., 1976. Segregation effects on consecutive competing reaction in a CSTR. *The Canadian Journal of Chemical Engineering*, 54(5), pp.572-577.
- Tu, J., Yeoh, G.H. and Liu, C., 2018. *Computational fluid dynamics: a practical approach*. Butterworth-Heinemann.
- Tuckerman, L.S., 2014. Taylor vortices versus Taylor columns. Journal of Fluid Mechanics, 750, pp.1-4.
- Tung, H.H., 2013. Industrial perspectives of pharmaceutical crystallisation. Organic Process Research & Development, 17(3), pp.445-454.
- Tung, H.H., Paul, E.L., Midler, M. and McCauley, J.A., 2009. *Crystallisation* of pharmaceuticals: an industrial perspective. Wiley.
- Valente, I., Celasco, E., Marchisio, D.L. and Barresi, A.A., 2012. Nanoprecipitation in confined impinging jets mixers: Production,

characterization and scale-up of pegylated nanospheres and nanocapsules for pharmaceutical use. *Chemical engineering science*, 77, pp.217-227.

- Versteeg, H.K. and Malalasekera, W., 2007. *An introduction to computational fluid dynamics: the finite volume method*. Pearson education.
- Vicum, L., Mazzotti, M. and Baldyga, J., 2003. Applying a thermodynamic model to the non-stoichiometric precipitation of barium sulfate. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 26(3), pp.325-333.
- Vilardi, G., Stoller, M., Verdone, N. and Di Palma, L., 2017. Production of nano Zero Valent Iron particles by means of a spinning disk reactor. *Chemical Engineering Transactions*, 57, pp.751-756.
- Villermaux, J. and David, R., 1983. Recent advances in the understanding of micromixing phenomena in stirred reactors. *Chemical Engineering Communications*, 21(1-3), pp.105-122.
- Villermaux, J. and Devillon, J.C., 1972. Representation de la coalescence et de la redispersion des domaines de segregation dans un fluide par un modele interaction phenomenologique. Proceed, 2nd Inc. In Symp. Chem. React. Engng., Amesterdam.
- Villermaux, J. and Falk, L., 1994. A generalized mixing model for initial contacting of reactive fluids. *Chemical Engineering Science*, 49(24), pp.5127-5140.
- Villermaux, J., 1990, November. Micromixing and chemical reaction semiquantitative criteria based on comparison of characteristic time constants. In AIChE Meeting, Chicago.
- Wang, H., 2015. Experimental and numerical study of Taylor-Couette flow (Doctoral dissertation, Iowa State University, Iowa).

- Wang, H., Mustaffar, A., Phan, A.N., Zivkovic, V., Reay, D., Law, R. and Boodhoo, K., 2017. A review of process intensification applied to solids handling. *Chemical Engineering and Processing: Process Intensification*, 118, pp.78-107.
- Wang, L., Marchisio, D.L., Vigil, R.D. and Fox, R.O., 2005. CFD simulation of aggregation and breakage processes in laminar Taylor–Couette flow. *Journal of Colloid and Interface Science*, 282(2), pp.380-396.
- Wang, M.L., Huang, H.T. and Estrin, J., 1981. Secondary nucleation of citric acid due to fluid forces in a Couette flow crystallizer. *AIChE Journal*, 27(2), pp.312-315.
- Wei, Y., 2017, December. The development and application of CFD technology in mechanical engineering. In *IOP Conference Series: Materials Science and Engineering* (Vol. 274, No. 1, p. 012012). IOP Publishing.
- Wenger, K.S., Dunlop, E.H. and MacGilp, I.D., 1992. Investigation of the chemistry of a diazo micromixing test reaction. AIChE Journal, 38(7), pp.1105-1114.
- Wenzel, D. and Górak, A., 2018. Review and analysis of micromixing in rotating packed beds. *Chemical Engineering Journal*, *345*, pp.492-506.
- Wojtalik, M., Bojarska, Z. and Makowski, Ł., 2020. Experimental studies on the chemical wet synthesis for obtaining high-quality MoS2 nanoparticles using impinging jet reactor. *Journal of Solid State Chemistry*, 285, p.121254.
- Wong, S.H., Ward, M.C. and Wharton, C.W., 2004. Micro T-mixer as a rapid mixing micromixer. Sensors and Actuators B: Chemical, 100(3), pp.359-379.
- Wu, G., Zhou, H. and Zhu, S., 2007. Precipitation of barium sulfate nanoparticles via impinging streams. *Materials Letters*, *61*(1), pp.168-170.

- Wu, H. and Patterson, G.K., 1989. Laser-Doppler measurements of turbulentflow parameters in a stirred mixer. *Chemical Engineering Science*, 44(10), pp.2207-2221.
- Wu, K., Wu, H., Dai, T., Liu, X., Chen, J.F. and Le, Y., 2018. Controlling nucleation and fabricating nanoparticulate formulation of sorafenib using a high-gravity rotating packed bed. *Industrial & Engineering Chemistry Research*, 57(6), pp.1903-1911.
- Xia, B. and Sun, D.W., 2002. Applications of computational fluid dynamics (CFD) in the food industry: a review. *Computers and Electronics in Agriculture*, 34(1-3), pp.5-24.
- Yang, F., Zhou, S. and An, X., 2015. Gas–liquid hydrodynamics in a vessel stirred by dual dislocated-blade Rushton impellers. *Chinese Journal of Chemical Engineering*, 23(11), pp.1746-1754.
- Yang, H.J., Chu, G.W., Zhang, J.W., Shen, Z.G. and Chen, J.F., 2005. Micromixing efficiency in a rotating packed bed: experiments and simulation. *Industrial & Engineering Chemistry Research*, 44(20), pp.7730-7737.
- Yang, T., Segets, D., Thajudeen, T., Han, Y. and Peukert, W., 2018. The effect of mixing on silver particle morphology in flow synthesis. *Chemical Engineering Science*, 192, pp.254-263.
- Yoon, H.S., Sharp, K.V., Hill, D.F., Adrian, R.J., Balachandar, S., Ha, M.Y. and Kar, K., 2001. Integrated experimental and computational approach to simulation of flow in a stirred tank. *Chemical Engineering Science*, 56(23), pp.6635-6649.
- Yu, S., 1993. *Micromixing and parallel reactions* (Doctoral dissertation, ETH Zurich).

- Zhou, M., Bai, D., Zong, Y., Zhao, L. and Thornock, J.N., 2017. Numerical investigation of turbulent reactive mixing in a novel coaxial jet static mixer. *Chemical Engineering and Processing: Process Intensification*, 122, pp.190-203.
- Zoulalian, A. and Villermaux, J., 1970. An experimental investigation of the state of mixing of the fluid in a chemical reactor. *The Chemical Engineering Journal*, *1*(1), pp.76-78.
- Zoulalian, A. and Villermaux, J., 1974. Influence of chemical parameters on micromixing in a continuous stirred tank reactor. *Advances in Chemistry*, 133, pp.348–361.
- Zoulalian, A., 1973. *Etude par voie chimique du micro-mélange dans un réacteur agité continu en phase liquide* (Doctoral dissertation, Université de Nancy I, Nancy).
- Zwietering, T.N., 1959. The degree of mixing in continuous flow systems. *Chemical Engineering Science*, *11*(1), pp.1-15.
CHAPTER 2

INTERFACIAL PHENOMENA IN THE SYNTHESIS PROCESS OF BARIUM SULFATE PARTICLES PRECIPITATED IN A LOBED INNER CYLINDER TC REACTOR: EFFECTS OF FLUID DYNAMICS

SUMMARY

Barium sulfate is a promising material, which has various usage in many industrial fields, such as pigment, filler and fibre reinforced composite (Patel et al., 2012). Such material is often chosen as a model substance to investigate the crystallization process affected by other operating parameters due to its rather clear chemical reaction kinetics (Petrova et al., 2008). Therefore, the reactive precipitation system of barium sulfate particles was employed to carry out the fundamental study in the TC reactor. In this chapter, three different kinds of morphology with various sizes of barium sulfate particles were produced by reactive precipitation in a lobed inner cylinder assembled TC reactor. It is found that particle morphology transition is strongly related to the hydrodynamics in the reactor, clearly indicating an interfacial interaction between feed solutions and aggregated particles. At low concentration, particle morphology transition is observed at the onset of turbulent TC. Such morphology transition also appears at the onset of turbulent Taylor vortex flow at high concentration. Based on different transition status, supersaturation is found to play an important role in nucleation and growth processes. In addition, it is revealed that the

synthesized particle reduces its size as the consequence of the transition in particle morphology, indicating the effect of variation of the feeding rates. Experimental results have confirmed that controllable synthesis of barium sulfate particles with a particular morphology can be achieved through suitable selection of the controlling parameters such as the rotational speed of inner cylinder, reactant feeding rate and supersaturation ratio.

2.1 Introduction

Precipitation is a traditional industrial process to produce solid particles. It has been used in many applications. Typical examples can be found in fabrication of pigments, ceramics, pharmaceuticals and bio-chemicals among others. For various purposes, the requirements of particle property are different. As particle size and morphology play important roles in determining particle property (Tai and Chen, 1998), many previous studies have paid attention to realization of particle size distribution control and to acquirement of a particular morphology (Tai and Chen, 1995; Jung et al., 2000; and Akyol and Cedimagar, 2016). As many factors can affect final particle property, such as reactant concentration, feeding modes, additives, reactor system, their interrelationships are complicated so that many precipitation mechanisms have been proposed (Judat and Kind, 2004). However, none of these proposed precipitation mechanisms can fully address the dynamic processes involved for synthesis of the particles in a particular reactor system. The present work focuses on the effects of three main parameters, rotational speed, feeding rate and supersaturation when employing a TC reactor for synthesis of particles on the change of particle morphology, in particular investigating barium sulfate system. Even though the synthesis of barium sulfate particles has been extensively studied (Aljishi *et al.*, 2013; Farahani *et al.*, 2017; and Wu *et al.*, 2007), controllable synthesis of the particles is still not fully understood, which requires further investigations.

Barium sulfate is a sparingly soluble salt, whose crystallization kinetics has been widely studied. Also, its precipitation system from aqueous barium chloride and sodium sulfate is available according to a series of studies by Nielsen (Nielsen, 1957, 1958, and 1959). In terms of particle morphology, a number of studies have been conducted to investigate different aspects of the potential possible factors. Many morphologies were observed in connection with the synthesis processes, involving tabular particles (or flat particles), dendritic particles, round-shaped particles (or spherical particles), rhombic particles and rice-shaped particles. Barresi et al. (1999) produced barium sulfate particles in a continuous Couette reactor, and they observed dendritic tabular crystals and tabular crystals with pyramidal by changing supersaturation, rotational speed and internal diameter of inner cylinder at the same time. They suggested that supersaturation is the dominant factor in determining particle morphology and size. However, they failed to reveal the effect of each individual variable. Marchisio et al. (2002) found a series of morphology change from tabular particles, then dendritic particles to rounded-shaped particles with increase of sodium sulfate concentration. They indicated that the excess of species has a stronger effect on particle morphology due to the preferential absorption of the excess ion. The effect of additives, such as EDTA, phosphate, lanthanum have been widely investigated experimentally in their study. From the results as reported by Li et al. (2016), various morphologies of barium sulfate particles are exhibited when treatment is done by using polyacrylic acid, such as ellipsoids, monodisperse spheres and rose-like

aggregates. They contributed the occurrence of these morphologies to the interactions between carboxyl groups of the additive and inorganic ions. However, the mechanism of randomly coiled conformation of the additive was not clearly illustrated, which results in controllable preparation of each morphology in industrial application to be still questionable. By means of barium sulfate precipitation system, Baldyga and his co-workers have experimentally conducted a number of studies using the mixing tank and numerically explored the mixing behaviour, aiming at fundamentally revealing the mechanism involved (Baldyga et al., 1995; Baldyga and Orciuch, 1997; and Phillips et al., 1999). During this process, they found that various parameters, including feed volume ratio, stirred speed, feeding time, volume ratio, initial concentration and stoichiometric ratio have impacts on particle size distribution and morphology. Also, they proposed a mixing-precipitation model which reasonably described the interaction between the micro-mixing time scale and reaction time scale, consistent with the experimental results. Pagliolico et al. (1999) have also illustrated the effect of the mixing on the production of various morphologies of barium sulfate, including dendritic particles, tabular particles, rose aggregates. They proposed shape factors for qualitative description of different morphologies. It can be seen that the above mentioned studies have focused on the effect of both solution conditions (typically excessive species, additives or supersaturation) and operating parameters (typically stirred speed, feeding point location, or addition time) on particle properties. However, most of deductions in these studies only focused on the change of particle size with the parameters as mentioned while the obtained results just showed the morphology for a particular condition. Little attention has been paid to how the morphology transits with respect to the variations of operating parameters and the correlations between the morphology and these parameters, in particular flow field environment and initial solution conditions.

TC reactor has been employed to prepare different kinds of particles due to its advantages (Jung et al., 2000; Aljishi et al., 2013; and Thai et al., 2015). As no stirrer is involved, the breakage of particles due to the elastic collision can be avoided. TC reactor consists of two co-axial cylinders, whose internal cylinder is rotating while the external cylinder is usually kept stationary. The typical characteristics of hydrodynamics of such reactor are a narrow shear rate distribution and relatively uniform kinetic energy dissipation. An increase in the rotational speed can effectively enhance the mixing efficiency. Jung et al. (2000) employed a TC reactor to prepare calcium carbonate particles in a gas-liquid system. After comparing the effects of species excess and shear stress, they suggested that the excessive species have a strong effect on synthesized particle size and morphology while the effect of flow dynamics on the synthesis can be negligible. It should be pointed out, however, that their analysis focused on the aspect of mass transfer, and overlooked the effect of shear rate variations. Mayra and Kim (2015) and Thai et al. (2015) have systematically conducted a series of studies on the synthesis of Ni-rich hydroxide crystals, a kind of cathode material for lithium ion battery, by using the TC crystallizer. They have clearly demonstrated that under the condition that the TC crystallizer operates in the range of the critical Reynolds number based on different gap sizes ($Re_c = 128.5$ -219.4), the formed Taylor vortices promote the mixing and enhance the mixing residual time, which yields the uniform agglomerate particles with high tap density. This clearly indicates that the hydrodynamics of the TC reactor will have a significant impact on the synthesis of particles and the particle crystals growth.

Even though reactive precipitation processes are very fast, Barresi et al. (1999) have demonstrated that mixing, especially micro-mixing, has a significant influence on the precipitation process itself. The mixing in mixing vessels that is caused by shear can be characterized by macromixing, mesomixing, and micro-mixing. According to engulfment-deformation-diffusion model (EDD) as proposed by Baldyga and Bourne (1984), engulfment due to the micromixing generates the local supersaturation and dilution of species. Such local supersaturation is the driving force for crystallization. Macromixing occurs on the scale of the reactor, functioning to convey the reactive solutions throughout the entire available space of the reactor (Vicum et al., 2003). Macromixing provides the environment for the following mixing processes, and affects the distribution of supersaturation. Mesomixing refers to the exchange of fresh feed and its surroundings on a coarse scale, lager than Kolmogorov scale, but smaller than integral scale of turbulence. It can influence micro-mixing by changing the local environment (Baldyga, 2016). Micro-mixing brings the fluid elements into contact, followed by molecular diffusion. It controls the generation of supersaturation.

It can be seen that the above mentioned studies that even for one particular substance, various particle monophonies can be synthesized by changing operating parameters or reactor types. However, many of these studies only focused on a single variable, little effort has been made to the combination of these factors together to reveal mechanism of particle morphology transition. Also, previous studies failed to propose mathematical models to correlate particle morphology and hydrodynamic parameters, which can be served as an indicator for industrial production. Therefore, the aim of this chapter is to investigate the morphology transition process by taking barium sulfate

precipitated in a TC reactor with a lobed internal cylinder (Li *et al.*, 2015) as an example. The effects of three parameters, rotational speed, feeding rate, and supersaturation, on the synthesized particle morphology are assessed and the correlations are obtained. In order to examine the effect of hydrodynamics characterized by shear rate which closely associates with the rotational speed, a wide range of rotational speeds were chosen varying from 25 to 1000 rpm. The interrelationship of shear rate and final particle morphology is acquired. Then, results will be discussed from the perspective of micro-mixing, as precipitation process is triggered by supersaturation, whereas micro-mixing controls the generation of local supersaturation. The experimental data obtained from current work can be used for the further validation of multiphase micro-mixing model.

2.2 Wettability and Interfacial Phenomena - Implications for barium sulfate particle precipitated using a lobed inner cylinder assembled TC reactor

The role of surface phenomena and contacts can play significant roles in the transitions of particle morphologies during precipitation. From the preceding section, it can be seen that the formation of different types of particles is related to interfacial phenomenon between liquid and particles. The effects of fluid behaviour on particles are embodied mainly from two aspects. On one hand, fluid flow in the reactor contributes to the interfacial ion concentration distribution, thus affecting the mass transfer to the aggregated crystal nuclei for formation of barium sulfate particles. Concentration gradient between nuclei surface (so referred to as equilibrium concentration) and bulk solution (so called bulk concentration) is the driving force for particle growth. During this process,

in spite of molecular diffusion, convection dispersion resulted from fluid flow has a dominant effects. Many previous studies (Brian et al., 1969; Kuboi et al., 1972; and Garside and Jančić, 1976) have adopted Sherwood number, defined as the ratio of convective mass transfer to diffusive mass transport, to characterise the mass transfer contributed from turbulence on fluid-particle interface for particle size ranging from macro-particles to micro-particles. This contribution comes from eddy fluctuation, thus indicating that the shear caused by turbulent eddies may play an important role in the formation of particles in the precipitation. Armenante and Kiwan (1989) proposed the correlation with Sherwood number for estimation of the mass transfer coefficient for description of the dissolution process of AgCl crystal. They have reaffirmed the effect of turbulence by applying different power input to the mixing tank reactor, and obtained an improved correlation between the Sherwood number and Reynold number. Furthermore, Jung et al. (2000) have obtained different calcium carbonate morphologies by changing the wall shear stress of the TC reactor used in their study. They interpreted this phenomenon from the point of view that ion adsorption takes place on the particle surface while the concentration gradient of adsorbed ions is also caused by shear stress. Thus, interfacial turbulence induced shear has an impact on aggregation. Bubakova et al. (2013) proposed an equation to describe the relationship between aggregate size and average shear rate of turbulent eddies formed in the mixing process. Similarly, for the process of Ni-rich hydroxide preparation, Mayra and Kim (2015) have also confirmed the parameters that are strongly associated with the fluid shear can have significant influence on agglomeration process. They have indicated that individual crystals can stack together to form irregular aggregates with fluid flow (mainly characterized by turbulent eddy motion), and then shear force generated by turbulent eddies can facilitate these aggregates to bind together to

form regular agglomerates. Thus, it may be concluded that interfacial ion concentration and interfacial fluid shear between the solution and particles have significant influences on particle growth and aggregation.

2.3 Theoretical modelling

2.3.1 Precipitation process dynamical model

The chemical reaction between aqueous solutions of barium chloride and sodium sulfate obeys the following equation,

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + 2NaCl_{(aq)}$$
(2.1)

The precipitation process of barium sulfate involves four main steps, nucleation, growth, agglomeration and breakup. The driving force of nucleation is supersaturation, which has effects on subsequent processes. Supersaturation σ is defined as the ratio of molar chemical potential φ (the molar Gibbs free energy) in supersaturated solution to the potential in saturated solution (Armenante and Kirwan, 1989), being expressed by the activities of ions, *a*,

$$\sigma = \frac{\varphi - \varphi_{eq}}{_{RT}} = ln \frac{a}{a_{eq}}$$
(2.2)

where a_{eq} is the activity in equilibrium, *R* is gas constant, and *T* is absolute temperature. The relationship between ion activity and concentration can also be described as follows:

$$a = \gamma_{\pm}c \tag{2.3}$$

where γ_{\pm} is the activity coefficient. Estimation of γ_{\pm} has been proposed by Debye-Huckel (1923), and the modified equation is usually adopted, given by

$$lg\gamma_{\pm} = -0.511z_{+}z_{-}\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2\sqrt{I}\right)$$
(2.4)

where z is the charge number, and I is the ionic strength, calculated by the following equation

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \tag{2.5}$$

where c_i is the molar concentration of species *i*. Since supersaturation is often expressed as the concentration difference Δc with saturation ratio *S* defined as the ratio of dissolved concentration to the equilibrium solubility and *Sa* as a relative saturation ratio, then

$$\Delta c = a - a_{eq} \tag{2.6}$$

$$S = \frac{a}{a_{eq}} = \sqrt{\frac{a_{Ba^{2+}}a_{SO_4^{2-}}}{K_{SP}}}$$
(2.7)

$$S_a = S - 1 \tag{2.8}$$

where K_{sp} is the solubility product of barium and sulfate ions in the equilibrium state (~ $1.1 \times 10^{-10} \text{ mol}^2/\text{L}^2$ at 20 °C). In the present work, we used *S* to describe the supersaturation of the system for the following calculation.

During precipitation, new particles are created by nucleation. Molecules of the reactants are combined to generate embryos when the energy required excesses energy barrier ΔG . During this process, there is an induction period which is the

necessary time to form a characteristic, significant number of nuclei. This time can also be regarded as the time elapsed from the mixing of reactants to the appearance of nuclei (Dirksen and Ring, 1991), an empirical expression for barium sulfate reaction (Carosso and Pelizzetti, 1984) can be used to estimate t_N

$$lgt_N = 15.5lg^{-2}S - 4.2 \tag{2.9}$$

Nucleation rate can be described using the following equation

$$J = k_N \Delta c^n \tag{2.10}$$

where *n* is the kinetic order of nucleation. In barium sulfate system, for $\Delta c < 0.01 \text{ mol/L}$, $k_N = 6 \times 10^{14}$, n = 1.775; for $\Delta c > 0.01 \text{ mol/L}$, $k_N = 2.53 \times 10^{39}$, n = 15 (Baldyga *et al.*, 1995).

Once nuclei have been formed, they start to grow to a particular shape and size. This process can be integrated into two steps: the mass transfer to the solidsolution interface, and the surface integration of growth units diffused into the crystal lattice. The total growth rate is given by

$$B = k_g (S - 1)^2 (2.11)$$

where k_g is growth coefficient. At a temperature of 20 °C, $k_g = 4 \times 10^{-11}$ m/s.

2.3.2 Taylor-Couette vortex flow

Flow pattern in a TC reactor can be characterized using the Reynolds number, defined by

$$Re = \frac{\omega_i r_i \delta_{eq}}{\nu} \tag{2.12}$$

where ω_i is the rotational speed of the inner cylinder, r_i is the equivalent radius of inner cylinder, estimated based on the ratio of four times of the inner cylinder cross-section area to the wetted perimeter of the cylinder, δ_{eq} is the equivalent gap between the inner cylinder and outer cylinder and ν is the kinematic viscosity of suspension, the ratio of the dynamic viscosity to the density of the fluid. The dynamic viscosity can be measured using a viscometer. For a fixed outer cylinder, with the increase of the rotational speed of inner cylinder exceeding a critical Reynolds number, the circular Couette flow becomes unstable, and Taylor vortices appear in pairs. Taylor vortex flow is a kind of secondary flow, superimposed on the laminar Couette flow. The velocity profiles of Couette flow and Taylor vortex are shown in Figure 2.1 respectively. Radial and axial velocities manifest once Taylor vortices appear.



Figure 2.1 (a) Azimuthal velocity profiles of circular Couette flow; (b) Axial velocity of Taylor vortex.

At low rotational speed, the driven flow can be considered as laminar Couette flow, and the fluid velocity is mainly determined by azimuthal velocity, as the highest radial and axial velocities are less than 15% of azimuthal velocity (Wereley and Lueptow, 1998). The azimuthal velocity profile in the gap for incompressible fluid takes the form of

$$u_{\theta} = Ar + \frac{B}{r} \tag{2.13}$$

where u_{θ} is the azimuthal velocity. A and B depend on the radius ratio $\eta = r_i/r_o$ and the cylinder angular velocity ratio $\zeta = \omega_o/\omega_i$.

$$A = \omega_i \frac{\zeta - \eta^2}{1 - \eta^2}, \quad B = \omega_i \frac{r_i^2 (1 - \zeta)}{1 - \eta^2}$$
(2.14)

Then, further increase in rotational speed leads to a series of instabilities occurs, changing from laminar flow including Taylor vortex flow, wavy Taylor vortex flow, modulated wavy Taylor vortex flow, to turbulent flow including turbulent Taylor vortex flow and fully developed turbulent Taylor flow. These flow patterns are influenced by the use of different aspect ratio and radius ratio. DiPrima *et al.* (1984) have summarized the effects of a series of radius ratio on flow patterns and some previous studies have investigated the transition points of these patterns (Desmet *et al.*, 1996; Takeda, 1999; and Haut *et al.*, 2003). At high rotational speed, radial and axial velocities cannot be ignored due to the enhanced effect of Taylor vortices. The mean velocity can be approximately estimated by

$$\bar{u} = \frac{2\omega_i r_i^2}{3(r_o^2 - r_i^2)} (r_i^3 + 2r_o^3 - 3r_i r_o^2)$$
(2.15)

2.4 Experimental

In the current work, the reactive precipitation of barium sulfate particles was realized with aqueous barium chloride and aqueous sodium sulfate. Barium chloride (BaCl₂·2H₂O) and sodium sulfate (Na₂SO₄) (analytical grade, Sinopharm Chemical Reagent Co., Ltd) were prepared with deionized water, respectively. Sodium pyrophosphate (analytical grade, Sinopharm Chemical Reagent Co., Ltd) was chosen as the dispersant, added into sodium sulfate, which corresponds to a 10% (w/w) theoretical yield of barium sulfate products. In order to remove solid impurities, all solutions were filtered with filter prior to the storage in containers.

The schematic diagram of experimental setup is shown in Figure 2.2 (a). Experiments were carried out in a TC reactor. It consists of two coaxial cylinders, where the plexiglass outer cylinder keeps static and the aluminium alloy inner cylinder rotates. The dimensions of the TC reactor employed in this study are described in Table 2.1, where the radius ratio is $\eta = r_i/r_o = 40.19/50.00 = 0.80$ and the aspect ratio is $\Gamma = L/\delta_{eq} = 300.00/9.81 = 30.58$. The total volume that can be used for reaction is 922 mL. According to Soos *et al.*'s study (2007), the use of lobed inner cylinder can eliminate or reduce low velocity or shear rate regions, thus improving mixing and mitigating the segregation of particles with different size and density. Therefore, a lobed inner cylinder is shown in Figure 2.2 (b). Due to the feature of lobed inner cylinder, the radius of the inner cylinder will change along the circumferential direction of the cylinder and an equivalent radius based on Equation (2.16) is used for evaluation of the gap between the inner and outer cylinders, i.e.

$$\delta_{eq} = \frac{2A_i}{R_i} \tag{2.16}$$

where A_i is the cross sectional area of the inner cylinder, and R_i is the perimeter.



Figure 2.2 (a) Schematic diagram of experimental setup for barium sulfate reactive precipitation in a TC reactor with the lobed inner cylinder; (b) Crosssection profile of both outer and inner cylinders.

 Table 2.1 Dimensions of the TC reactor.

Equivalent radius of lobed inner cylinder, r_i (mm)	40.19
Radius of outer cylinder, r_o (mm)	50.00
Gap size, δ_{eq} (mm)	9.81
Reactor length, L (mm)	300.00

All experiments were conducted at room temperature of 20 °C. Barium chloride served as the bulk solution, which was fed into the reactor firstly at the bottom of the reactor before the precipitation reaction takes place by peristaltic pump. The rotational speed of the inner cylinder was controlled by a servo motor, and feeding rate was well-controlled by a constant flow peristaltic pump. They have been carefully calibrated before the experiments. After the rotational speed was adjusted to a particular value, the flow was gradually developed to become steady and the feeding rate of both barium chloride and sodium sulfate solutions were adjusted to a required value and was then pumped into the reactor to induce the reaction. During each experiment, suspension samples were taken continuously from the outlet located at the top of the reactor for a certain time, and at the end of each run they were quickly diluted with deionized water to quench the reaction. After conducting each experiment, the reactor was cleaned by diluted hydrochloric acid to remove barium sulfate particles that have stuck on the wall of the reactor, then rinsed twice with deionized water. Collected samples were washed three times to sufficiently dissolve sodium chloride coproduced in the reaction and other excessive ions. Products were then filtered with mixed cellulose ester microporous membrane filter (pore size $0.22 \mu m$), dried in the oven at 100 °C for 24 hours. For even smaller particles, a 0.1 µm pore filter paper was used.

Three parameters were involved in these experiments, including rotational speed, feeding rate, and supersaturation. Two initial concentrations (i.e. two supersaturations) of reactants were prepared at 0.1 mol/L and 1 mol/L, respectively. At low concentration, rotational speed had a wide range from 25 rpm to 1000 rpm, and feeding rate changed from 5 mL/min to 80 mL/min. In total, 49 runs were carried out. At high concentration, rotational speed varied

from 50 rpm to 1000 rpm, and feeding rate changed from 5 mL/min to 60 mL/min. There were 32 runs were carried out. All parameters and their values have been summarized in Table 2.2. In addition, in order to ensure the repeatability of the experiments, some of the experiments were repeated at least twice.

	C_{BaCl_2}	C _{Na2} SO ₄	Rotational	Feeding rate (mL/min)
	(M)	(M)	speed (rpm)	
			25	5, 10, 15, 20, 40, 60, 80
			50	5, 10, 15, 20, 40, 60, 80
			100	5, 10, 15, 20, 40, 60, 80
Low	0.1	0.1	300	5, 10, 15, 20, 40, 60, 80
concentration			600	5, 10, 15, 20, 40, 60, 80
			800	5, 10, 15, 20, 40, 60, 80
			1000	5, 10, 15, 20, 40, 60, 80
			50	5, 10, 40, 60
			100	5, 10, 40, 60
			200	5, 10, 40, 60
High	1.0	1.0	300	5, 10, 40, 60
concentration			400	5, 10, 40, 60
			600	5, 10, 40, 60
			800	5, 10, 40, 60
			1000	5, 10, 40, 60

Table 2.2 Operating conditions.

Selected samples were then analysed by the scanning electron microscope (SEM, Sigma VP, ZEISS, Germany). Before taking the SEM observation, the samples were slightly ground. In order to increase the electrical conductivity, silicon wafer was stuck onto carbon tape. Barium sulfate particles were dispersed into ethanol, then dropped on the surface of silicon wafer. Prepared samples were dried in the oven about 10 minutes before conducting SEM observation. Particle size was measured and characterized by the software, Image J, which should establish a coordinate system based on the scale in SEM images. For each reaction condition, at least three images were selected, and 200 particles were measured in each image.

2.5 Results and discussion

As it has been mentioned before, final particle properties are influenced by many factors. With no additional additives in the system, the properties of particles are directly influenced by the surroundings where the crystals create and grow. Feeding rate affects the local amount of the fresh reactant fed to the system per unit time, which reflects the mesomixing efficiency in the TC reactor. Rotational speed controls the dispersion degree of fresh reactant, bringing the unpremixed reactants into contact at a molecular level. It reflects the micromixing efficiency of the system. Reactant concentration is the other factor that affects the formation of supersaturation of solution, resulting in the supersaturation being the driving force for the local nuclei formation. Thus, it can be suggested that particle morphology will be controlled by at least these three parameters.

The formation of different morphologies results from the mixing behaviour throughout the whole nucleation process, while mixing is caused by fluid shear. Fluid shear generating velocity gradient can re-disperse species, and create eddies. Thus, shear has significant effects on fluid flow behaviour, such as mixing and mass transfer. For a laminar flow, shear rate in the gap can be estimated from the derivative of Equation (2.13)

$$G = \frac{-du_{\theta}}{dr} = A - \frac{B}{r^2} \tag{2.17}$$

The lowest shear rate at outer cylinder wall and the highest shear rate at inner cylinder wall at laminar flow are shown in Table 2.3. Due to the narrow gap of the TC reactor, the shear rate difference between inner cylinder wall and outer cylinder wall is not significant. Therefore, shear rate in the TC reactor can be seen as uniform, which can be reasonably expressed by the average shear rate. This feature is also one good performance of this reactor. However, when fluid flow becomes turbulent, shear rate is not only dominated by tangential velocity due to the enhanced radial and axial velocities induced by Taylor vortex. Also azimuthal velocity is different from the one at laminar state. For turbulent Taylor vortex flow, the local shear rate caused by turbulent energy dissipation rate, given by

$$G = \sqrt{\frac{\varepsilon}{\nu}} \tag{2.18}$$

Table 2.3 Shear rate in laminar TC system.

Rotational speed	Inner cylinder wall	Outer cylinder	Average shear
(rpm)	shear rate (s ⁻¹)	wall shear rate (s ⁻¹)	rate (s^{-1})
25	12.17	9.56	10.87
50	24.35	19.11	21.73
100	48.70	38.23	43.46

The exact turbulent energy dissipation rate is difficult to determine but the mean turbulent energy dissipation can be estimated from the following equation for TC reactor (Kuboi *et al.*, 1972).

$$\langle \varepsilon \rangle = \frac{P}{m_l} = \frac{\pi L r_l^4 \omega_l^3 f}{V}$$
(2.19)

In addition, the friction factor *f* is given as a function of δ_{eq}/r_i and the Reynolds number (Atsumi *et al.*, 1988).

$$f = 0.80 \left(\frac{\delta_{eq}}{r_i}\right)^{0.35} Re^{-0.53}$$
(2.20)

The change of shear rate at different rotational speed for current study is shown in Figure 2.3. It can be seen from Figure 2.3 that shear rate has a sharp increase when the flow pattern changes from laminar flow into turbulent flow.



Figure 2.3 Shear rate at different rotational speeds.

2.5.1 Particle morphology at a low concentration of 0.1 mol/L

At a low concentration of 0.1 mol/L, the rotational speed were varied from 25 rpm to 1000 rpm with the feeding rate being given ranging from 5 mL/min to 80 mL/min. There were three kinds of particle morphology observed from the SEM images in the same magnification as shown in Figure 2.4. The appearance of these particles looks like flake, transition mode and granule, respectively. Figure 2.5 (a) shows the changes of morphology under the influence of the rotational speed and feeding rate. The obtaining of the transition mode particles was marked by connecting those data points that can be clearly distinguished from the other two states. It can be seen from the Figure 2.5 (a) that the flake particles are mainly formed at low rotational speed at low feeding rate. It is thus indicated from Figure 2.5 (a) that the flake particles are expected to be generated when applying the high feeding rate (the top left region of line AB)

and granule particles are formed with the high rotational speed (the bottom right region of line DE). However, it cannot be identified that whether or not there exists an intersection point with the development of line AB and line DE.



Figure 2.4 Three representative morphologies of barium sulfate particles at low concentration: (a) $\omega = 25$ rpm; Q = 20 mL/min, flake; (b) $\omega = 300$ rpm; Q = 40 mL/min, transition; (c) $\omega = 600$ rpm; Q = 5 mL/min, granule.



Figure 2.5 Morphology distribution at various rotational speeds (Reynolds numbers) and feeding rates at low concentration.

It has been suggested that beyond a transition Reynolds number at $Re_T=1.3\times10^4$, the flow in the reactor becomes turbulent Taylor flow (Lewis and Swinney, 1999), this corresponding to the rotational speed of 313 rpm (with the aspect ratio $\Gamma = 30.58$) in current study. From Figure 2.5 (a), transition state appears at the rotational speed of 300 rpm, which is in a good agreement with the transition to turbulent Taylor flow as predicted.

2.5.1.1 Mechanism of granule particles formation

The formation of granule particles with high rotational speed can be explained in terms of the mixing efficiency and agglomerative bonding force. It can be seen from Figure 2.5 (a) that the minimum value of rotational speed at which granule particles appear is 600 rpm, and the flow has already developed into fully turbulent Taylor flow. Also, the feeding rate is low enough to form granule particles at this point. As micro-mixing of the fresh feed and bulk solution has significant effects on the final products, the mixing process of two solutions can be explained by the micro-mixing model. Many theoretical models have been proposed to describe the micro-mixing behaviour in the reactors, such as diffusion model (Mao and Toor, 1970), deformation-diffusion model (Ottino *et al.*, 1979), eddy engulfment model (Baldyga and Bourne, 1984), and incorporation model (Fournier *et al.*, 1996). Among these models, the engulfment model proposed by Baldyga and Bourne (1984) has been widely adopted. The engulfment rate is defined as

$$E = 0.058 \left(\frac{\varepsilon}{\nu}\right)^{1/2} \tag{2.21}$$

Based on this model, two species are considered as two shrinking slabs (Baldyga *et al.*, 1995). In case of turbulent Taylor vortex flow, once the fresh reactant Na₂SO₄ has been added into the TC reactor, two reactant slabs are in contact and interact each other with the turbulent eddies being stretched due to turbulent vorticity and generating a local turbulent shear. The scale of eddies can be approximately considered as being proportional to Kolmogorov length scale, defined by

$$\lambda_{eddy} = C_{eddy} \left(\frac{\nu^3}{\varepsilon}\right)^{1/4} \tag{2.22}$$

Fluid velocity fluctuation increases with intensified turbulence. More small eddies generate and dissipate. It can be seen from Equation (2.22) that the length scale is reduced with the increase of energy dissipation rate. The incorporation of fresh feed after finishing the processes of engulfment and deformation will finally become small fluid elements, smaller than Kolmogorov length scale. Accordingly, at high rotational speed, the contact area between fresh solution and bulk solution increases, leading to the acceleration of the molecular diffusion. The characteristic diffusion time can be estimated according to Baldyga and Bourne (1986), given by

$$t_D = 2\left(\frac{\nu}{\varepsilon}\right)^{1/2} \operatorname{arcsinh}(0.05S_C)$$
(2.23)

where *Sc* is Schmidt number. Based on this model, the characteristic time by engulfment on the course of mixing is roughly equal to E^{-1} ,

$$t_m = 12 \left(\frac{\nu}{\varepsilon}\right)^{1/2} \tag{2.24}$$

In our experiment, this characteristic time (estimated to range from 0.711 to 0.0075 s based on different rotational speed) was about 17 times larger than diffusion time (estimated to range from 0.041 to 0.0004 s). Therefore, it is suggested that the engulfment may control the micro-mixing process which can be seen as the rate-determining step and t_m can be seen as the typical micro-mixing time.

The time constants are of importance in assessing the influence of mixing on reactive precipitation. It has been suggested by Baldyga (2016) that when the mixing time, t_m is shorter than the induction time t_N , $t_m < t_N$, nucleation step cannot be affected by mixing intensity, as the local region has uniformly dispersed with reactants before nucleation. While when $t_m > t_N$, nucleation would occur in a non-uniform region. Under this condition, the effect of mixing on precipitation can be crucial. Since the BaSO₄ reactive precipitation is fast by nature, reactants contact quickly once the Na₂SO₄ has been added into the TC reactor, resulting in the generation of local supersaturation. Then, nuclei are formed in the duration of induction. The induction time was about 0.0014 s, which was smaller than the micro-mixing time 0.0075 s at 1000 rpm. Therefore, reactive precipitation can be controlled by mixing condition achieved by fluid shear. Because the induction period is independent with the micro-mixing process, the precipitation reaction takes place and the rest of fresh reactants is incorporated and diffused into the vortices at the same time. Therefore, the maximum nucleation rate attains at the first contact of two species due to the dilution of supersaturation. This in fact indicates that after a number of nuclei are formed, the growth rate decreases with the reduced supersaturation as there is little amount of reactant left for nuclei to grow further.

At the end of the primary process of crystallization, secondary process takes place, having a determining effect on particle qualities. Nuclei grow into grains then crystallites. This process is dependent on the mass transfer, while mass transfer is caused by interfacial concentration gradient. Convective mass transfer and diffusive mass transfer coexist in the system simultaneously. Here the Sherwood number, *Sh* derived by Armenante and Kirwan (1989) as a function of Reynolds number and Schmidt number can be used to illustrate the interfacial mass transfer during nuclei growth.

$$Sh = 2 + 0.52Re^{052}Sc^{1/3}$$
(2.25)

As granule particles are formed at a relative high rotational speed, an increase in Sherwood number indicates an enhanced convection mass transfer from bulk solution to solid surface. It can be deduced that an intensified interfacial mass transfer can facilitate the formation of granular particles. Additionally, Peclet number, *Pe* is used here to determine the dominant effect on the interaction among particles, expressed as a function of Reynolds number and Schmidt number which is given by

$$P_e = R_e S_C = \frac{r_i \omega_i \delta_{eq}}{D} \tag{2.26}$$

where *D* is the diffusion coefficient, including the effects of Brownian motion and molecular diffusion. The range of *Pe* applicable in the present experiments was $9.7 \times 10^5 < Pe < 3.9 \times 10^7$, which was much greater than 1 (*Pe* >> 1). Larger *Pe* values indicate that the particle collision is dominated by the convective mass transfer due to Taylor turbulent eddy transport. Such convection effect can also be improved by the intensification of turbulent eddies, realized by increasing the rotational speed of the inner cylinder.

Due to the entrainment of these crystallites by the turbulent eddies, the selfassembled aggregation makes them closer, leading to the agglomeration of crystallites which further results in the formation of final particles. In Aljishi *et al.*'s study (2013), they described crystallites as the primary grains and final particles as the secondary grains. The joint effect of micromixing and crystallization on the formation of the particles and its mechanism are illustrated in Figure 2.6. For powder-like particle preparation, agglomeration becomes an important growth mechanism due to a large number of nuclei created. The final particle morphology is a result of the relative rates of chemical reaction, nucleation, growth and agglomeration. During this process, the motion of two or more crystallites in suspension makes them closed and then aggregate. Furthermore, once the crystals have stayed together for a sufficient long time, the agglomerative bonds can be formed due to intergrowth (Brunsteiner *et al.*, 2005). An empirical formulation of the net agglomeration rate (including bond making and breaking) was proposed

$$K_{aggl} = \beta_{aggl} \varepsilon^p S^q f(l_m, l_n) \tag{2.27}$$

where β_{aggl} is agglomeration efficiency, l_m and l_n denote the sizes of the binary agglomerating particles. It can be seen clearly from this equation that the agglomeration rate is influenced by the turbulence dissipation rate and supersaturation. Therefore, for a given rotational speed, the average shear rate is a constant while along with the nucleation process based on our analysis before, the supersaturation is reduced. This can then result in the reduction of agglomeration rate. Accordingly, the particle size cannot increase continuously as the agglomeration rate reaches its limit at a given condition. This is consistent with the results obtained in the experiments. At granule state, particle morphologies are similar and their size were kept at around 180 nm to 200 nm no matter the change of rotational speed. This result is consistent with the finding of Dehkordi and Vafaeimanesh (2009). They also obtained a constant final particle size. Moreover, especially at high rotational speed of 1000 rpm, application of the higher feeding rate can still promote the generation of granule particles because at this feeding rate, the mass dispersed is saturated while the reaction process remains the same, thus resulting in the particle size unchanged. This can explain why the particle morphologies and sizes are similar at granule state no matter how the feeding rate and rotational speed change.



Figure 2.6 Mechanism of particle formation in fluid.

In addition, at transition state, we also measured the particle size, and found that the particle size exhibits a reduction trend with increase in the rotational speed at a constant feeding rate as shown in Figure 2.7. Based on the Reynolds number

calculated before, at the rotational speed of 300 rpm, turbulent Taylor vortex flow has been formed. Particle morphology shows a significant difference from the previous large blocks with irregular shape. The rotational speed of 300 rpm almost corresponds to the point where turbulent Taylor vortex flow began to form. Thus, the disturbance effect of feeding rate cannot be ignored. Fluid is sensitive to any small perturbation, as this perturbation will lead to big velocity fluctuation, then create small eddies. Aljishi *et al.* (2013) observed in their experiment that with increase in axial flow intensity, the onset of flow pattern instability is significantly delayed. Also, it can be seen from Figure 2.5 (a) that at 600 rpm, the beginning point of granule particles formation are observed at a low feeding rate, where the disturbance effect is weak. Therefore, it is suggested that the appearance of particle size reduction trend can be seen as an indicator for morphology transition.



Figure 2.7 Change of particle size with rotational speed (Reynolds number) at transition state at low concentration.

2.5.1.2 Mechanism of the formation of flake particles

It can be clearly seen from Figure 2.4 (a) that the formation of big flake particles results from the stable agglomeration of smaller particles. The blurred boundary marked at point 1 and the small particles attached at point 2 indicate that the big flake particle is the product of small particles aggregation then agglomeration or level by level accumulation. This formation process is strongly influenced by the flow dynamics. In order to elaborate on this phenomena, Figure 2.8 shows the morphology of the formed flake particles at various rotational speeds. Figure 2.8 (e) also shows the transition mode particles for comparison.



Figure 2.8 Development of the flake particles with increase of the rotational speed: (a) $\omega = 0$, flake; (b) $\omega = 25$ rpm, flake; (c) $\omega = 50$ rpm, flake; (d) $\omega = 100$ rpm, flake; (e) $\omega = 300$ rpm, transition. Note: the magnification of image (a) is 2.00k, and the others are 20.00k.

Firstly, many small particles are formed and suspend in the mixture solution. When low rotational speed is applied, the entrainment on the fresh feed by eddies is not strong and the formed particles can disperse quite uniformly. Because at laminar state, velocity is dominated by azimuthal velocity. The effect of Taylor vortex is not significant. Therefore, mixing behaviour is not strong. Accordingly, the contact area between the bulk solution and the fresh feed is not big enough instead more mass being transferred to the formed small particle surface, leading to the local accumulation. The length scale of particles is smaller than minimum vortex scale. Fluid shear induced by the velocity gradient acted on particle agglomeration. Therefore, the small particles generated under this condition are still larger than those in high rotational speed. Also, weak shear decreases the engulfment of bulk solution and fresh feed, which means the exchange between the bulk solution entrained by eddies and fresh feed is poor at the inlet. This phenomenon becomes notable at a high feeding rate. For a particular small region, enhanced collision can promote the generation of agglomeration bonds. This kind of agglomeration is gradually reduced as shown from Figure 2.8 (b) to Figure 2.8 (e), consistent with the analysis above. It should be noted that as can be seen from Figure 2.8 (a) where there is no influence of the turbulent eddies due to zero rotational speed of the inner cylinder, few formed small particles can be still observed. At this condition, the droplets of fresh Na₂SO₄ feed directly contact with bulk BaCl₂ solution from the inlet and are diffused into the bulk solution, the reactive product as agglomerated big flakes sinks to the bottom of reactor. This is likely caused by a local saturated diffusion in which many formed small particles agglomerate to form the big flakes.

Secondly, the effect of eddy shear on flake particles is different from granule particles. At high rotational speed, micro-mixing takes place at Kolmogorov length scale, which is larger than the size of granule particles. Therefore, larger turbulent eddies only affect the mixing process of two species, indicating that the particles passively follow the vortex motion. Here we use Stokes number, *St* to describe the trapping of particles by an eddy (Crowe *et al.*, 1996).

$$St = \frac{\rho_p d^2 u_t}{18\mu l} \tag{2.28}$$

where u_t is the terminal velocity of particles (Haider and Levenspiel, 1989), and *l* is the suitable length scale for the vortex. For small eddies in TC reactor, *l* can be chosen as Kolmogorov length scale for the calculation of St. At high rotational speed for the formation of granule particles with the diameter of 200 nm, St is approximately 1.1×10^{-4} , which is much smaller than 1.0. As indicated by Crow et al. (1979), St << 1.0 represents the case that particles are well following the eddy. However, for low rotational speed, Kolmogorov length scale increases, and the scale of formed flake particles is in the order of eddies. Vortex and flake particles are all at micron scales. Therefore, eddy shear strongly interacts with the flake particles. If shear force is strong enough, the size of flake particles will be smaller than Kolmogorov length scale as the particle surface will be ripped off. This is consistent with the observation from the semi-batch precipitation experiment of Baldyga et al. (1995) in which they suggested that rotational speed had no influence on particle size at a relatively weak turbulence. Barresi et al. (1999) also agreed with this argument from their variation coefficient analysis.

Based the analysis above, both rotational speed and feeding rate have effects on final particle morphology. Also, the transition region in Figure 2.5 (a) indicates an ellipse-like shape when the both parameters are combined. In order to obtain quantitative information about particle morphology, a fitting equation is proposed involving shear rate (rotational speed) and feeding rate, shown in Figure 2.5 (b).

$$0.33\dot{\eta}_V^2 - 0.51\dot{\eta}_V Q + 0.79Q^2 - 9.06\dot{\eta}_V + 6.02Q + 61.41 = 0 \qquad (2.29)$$

The relationship is expressed in a semi-natural log coordinate. In order to unify the dimension, shear rate here refers to the entire volume shear rate, $\dot{\eta}_V$ for the TC reactor, defined as

$$\dot{\eta}_V = GV \tag{2.30}$$

Equation (2.29) can be seen as an indicator for particle morphology. Inside the ellipse, transition mode takes place, while in the top left region of the ellipse, flake particles can be created, and in the bottom right region, granule particles are formed.

2.5.2 Particle morphology at a high concentration of 1.0 mol/L

In order to elaborate on this transition phenomenon, experiments at a higher concentration of 1.0 mol/L were also carried on. The rotational speed was varied from 50 rpm to 1000 rpm, and the feeding rate was changed from 5 mL/min to 60 mL/min. Three similar morphologies as at low concentration were observed as shown in Figure 2.9. Also, a transition region was identified to distinguish

the other two states as shown in Figure 2.10. Compared with that shown in Figure 2.5 (a) at 0.1 mol/L, the transition region is exhibited to be narrower while the beginning points and ending points fall into the range of relatively lower rotational speeds. Particle size at transition state were measured, also illustrating a reduction trend as shown in Figure 2.11. Thus, the size reduction can be considered as an indicator for morphology transition.



Figure 2.9 Three representative morphologies of barium sulfate particles at high concentration: (a) $\omega = 50$ rpm; Q= 5 mL/min, flake; (b) $\omega = 100$ rpm; Q= 5 mL/min, transition; (c) $\omega = 800$ rpm; Q= 10 mL/min, granule.



Figure 2.10 Morphology distribution at various rotational speeds (Reynolds number) and feeding rate at high concentration.



Figure 2.11 Change of particle size with rotational speed (Reynolds number) at transition state at high concentration.

At low concentration, the change of kinematic viscosity means the change of Reynolds number even at the same rotational speed. The kinematic viscosity at 1.0 mol/L is about 1.85 times as high as 0.1 mol/L. According to the radius ratio of $\eta = 0.80$, the critical Reynolds number to generate Taylor vortex flow is 97.33 (DiPrima *et al.*, 1984). The generation of turbulent Taylor vortex flow is at a Reynolds number ratio of $R = Re/Re_c \sim 35$ as indicated by Bubakova *et al.* (2013), corresponding to the rotational speed of 89 rpm. Therefore, turbulent Taylor vortex flow occurs at the rotational speed of 89 rpm, roughly corresponding to the beginning of transition state at 100 rpm in this case. Also, fully turbulent flow is formed at the rotational speed of 581 rpm, roughly corresponding to the ending of transition is correlated with the flow patterns in the reactor. Based on engulfment model, a good mixing of two species needs high energy input. As mentioned earlier, formation of flake particles is the result of the poor dispersion of reactants. When the transition was observed, the micro-mixing

was improved. In the present work, the transition state was observed at least under the condition of turbulent flow.

2.5.3 Influence of the low concentration and high concentration on particle formation

It is noticed that the onset of the transition state is different for different concentrations. At low concentration, transition state was observed at turbulent flow regime at 300 rpm while at high concentration, such transition appears at turbulent Taylor vortex flow regime at 100 rpm. Also, the transition range becomes smaller at high concentration. To keep the Reynolds number unchanged, the increase in kinematic viscosity means that the rotational speed has to be increased to maintain the same fluid pattern. This implies that the transition state should be observed at a higher rotational speed than that in low concentration. Also, based on the mechanism of various morphologies formation at low concentration, the onset of turbulent flow is essential for the creation of transition particles. However, at high concentration, transition state appeared at a much lower rotational speed. The final granule particle size at high concentration was approximately measured as 130 nm to 150 nm, which is smaller than that at low concentration.

The above observed results should also result from the increase in local supersaturation, which was the only varying parameter in the comparison experiments. Since the nucleation and growth are directly dependent on supersaturation, the effect of supersaturation is crucial on morphology transition. As can be seen from Equations (2.10) and (2.11), the order of magnitude of nucleation rate is much higher than growth rate, indicating that nucleation is
more sensitive to supersaturation than growth. Many studies have been suggested that an increase in supersaturation may result in the nucleation process to be dominant (Barresi et al., 1999). In the experiments of Barresi et al. (1999) and Marchisio et al. (2002), they all observed tabular particles to form at low concentration and dendritic particles at high concentration. Baldyga et al. (1995) suggested that the formation of tabular shape is the consequence of surface nucleation, leading to the overgrowth of crystal surface. While with improvement of flow environment (increasing flow rate in jet) round-shaped particles can form (Marchisio et al., 2002). In our experiment, granule particles were observed with the increase of the rotational speed (likely corresponding a strong local turbulent shear due to the turbulent eddies). Since with the increase in supersaturation, the mass brought into the system is more than that at low supersaturation for the same small droplets. In such environment, the available reactant molecules mainly function to form nuclei. Thus, the nucleation significantly increases. It is thus concluded that a higher nucleation rate facilitates the creation of a large number of nuclei which is beneficial to the formation of small particles. On the other hand, as mentioned in Section 2.5.1.1, an increased interfacial concentration gradient can facilitate the formation of granular morphology. Therefore, in general, a high supersaturation results in the formation of small granule particles. It should be noticed that agglomeration is an important part on the course of nucleation. It is usually significant at low mixing rate (Dehkordi and Vafaeimanesh, 2009). At low rotational speed, agglomerative bonding force is strengthened due to weak shear and large vortex scale, more primary crystallites agglomerate to form large flake particles as discussed earlier. It can thus be inferred that the supersaturation can be seen as a primary factor in determining particle morphology while the effect of agglomeration is the second place but it cannot be ignored at low rotational

speed. Furthermore, from the analysis of particle formation mechanism mentioned above, the creation of agglomerative bonds requires a close distance and sufficient long time. With the increase of rotational speed, fluid motion becomes more significant. The formation of agglomerative bonds was reduced, followed with the number decrease of crystallites to agglomerate. Therefore, it is suggested that the appearance of particle size reduction trend can be seen as an indicator for morphology transition.

Based on the analysis and discussion above, it can be suggested that when using TC reactor for synthesis of the particles, mixing affects the whole process especially for the mixing of individual reactant solution through the engulfment and the subsequent chemical reaction. Supersaturation has the effect on crystallization process when reactants are in contact but this effect may surpass the flow environment. It is conjectured that agglomeration can be seen as a consequence of flow dynamics and supersaturation when working on crystallites. Last but not the least, interfacial phenomenon between liquid and solid particles exists throughout the whole precipitation process. It includes mainly two aspects. One is from the interfacial concentration distribution, which determines the mass transfer process from liquid to solid, thus nuclei growth process, and the other is the surface treatment of fluid shear on final agglomerates.

2.6 Conclusions

In the present work, a TC reactor was employed for the purpose of controllable production of barium sulfate particles with various morphologies. The morphologies obtained include flake particles, transition particles and granule particles. During the reactive precipitation process, three main control parameters were assessed. The presence of a particular morphology results from the combined effect of these parameters. For different solution conditions, the influence of fluid dynamic environment inside the TC reactor on particle morphology may change. In general, morphology transition is suggested to be related to the change of flow pattern that the turbulent eddies strongly interact with the particle crystals. Considering the joint effect of fluid dynamics and supersaturation, it can be deduced that micro-mixing caused by fluid shear plays a primary role in species dispersion, which determines the formation of various morphologies, while the supersaturation controls the crystallization process, which determines the onset of transition state. Both fluid shear and supersaturation can finally affect the interfacial concentration distribution, thus particle growth. Then particle agglomeration can be controlled by interfacial shear force. It is thus concluded that interfacial phenomenon plays significant roles in the transition of particle morphologies during precipitation. More specifically, the following conclusions have been drawn from the current study:

(1) At low supersaturation, the morphology transition mode is observed at fully developed turbulent Taylor flow, and it appears at turbulent Taylor vortex flow at high concentration. It is indicated that turbulent shear creating isotropic small eddies can assist controllable synthesis of particles, which results in the generation of relatively regular morphology. This is due to the enhanced mixing intensity and interfacial mass transfer caused by shear at turbulent flow. However, anisotropic vortex shear in laminar state has the potential to create irregular particle morphology. On the other hand, agglomeration as a part of crystallization, can be enhanced by both low mixing intensity and high supersaturation, leading to the formation of flake particles.

(2) The decrease in particle size with the increase of rotational speed at transition state results from the disturbance effect of the feeding rate. Fluid is sensitive to any small perturbation especially at high rotational speed, then more small isotropic eddies will be created.

(3) Comparing the transition results at both low and high concentrations, supersaturation will lead itself to the formation of smaller particles, and the transition at lower rotational speed. Although the use of high supersaturation can increase the agglomeration for a given rotational speed, it facilitates the formation of a large number of nuclei but leaves little mass for further particle growth. A high interfacial concentration also enhances the mass transfer between fluid and solid particles. Thus, it can be inferred that the supersaturation has a stronger effect than the agglomeration in determining the particle morphology.

References

- Akyol, E. and Cedimagar, M.A., 2016. Size and morphology controlled synthesis of barium sulfate. *Crystal Research and Technology*, 51(6), pp.393-399.
- Aljishi, M.F., Ruo, A.C., Park, J.H., Nasser, B., Kim, W.S. and Joo, Y.L., 2013. Effect of flow structure at the onset of instability on barium sulfate precipitation in Taylor–Couette crystallizers. *Journal of Crystal Growth*, 373, pp.20-31.
- Armenante, P.M. and Kirwan, D.J., 1989. Mass transfer to microparticles in agitated systems. *Chemical Engineering Science*, *44*(12), pp.2781-2796.
- Atsumi, K., Makino, T., Kato, K., Murase, T., Iritani, E., Chidphong, P. and Shirato, M., 1988. Frictional resistance of grooved rotor in cylindrical dynamic filter chamber without permeation or throughflow. *Kagaku Kogaku Ronbunshu*, 14(1), pp.14-19.
- Baldyga, J., 2016. Mixing and fluid dynamics effects in particle precipitation processes. *KONA Powder and Particle Journal*, *33*, pp.127-149.
- Baldyga, J. and Bourne, J.R., 1984. A Fluid Mechanical Approach to Turbulent Mixing and Chemical Reaction Part III Computational and Experimental Results for the New Micromixing Model. *Chemical Engineering Communications*, 28(4-6), pp.259-281.
- Baldyga, J. and Bourne, J.R., 1986. Principles of micromixing. *Encyclopedia of fluid mechanics*, *1*, pp.147-201.
- Baldyga, J. and Orciuch, W., 1997. Closure problem for precipitation. *Chemical Engineering Research and Design*, 75(2), pp.160-170.

- Baldyga, J., Podgórska, W. and Pohorecki, R., 1995. Mixing-precipitation model with application to double feed semibatch precipitation. *Chemical Engineering Science*, 50(8), pp.1281-1300.
- Barresi, A.A., Marchisio, D. and Baldi, G., 1999. On the role of micro-and mesomixing in a continuous Couette-type precipitator. *Chemical Engineering Science*, 54(13-14), pp.2339-2349.
- Brian, P.L.T., Hales, H.B. and Sherwood, T.K., 1969. Transport of heat and mass between liquids and spherical particles in an agitated tank. AIChE Journal, 15(5), pp.727-733.
- Brunsteiner, M., Jones, A.G., Pratola, F., Price, S.L. and Simons, S.J., 2005. Toward a molecular understanding of crystal agglomeration. *Crystal Growth & Design*, 5(1), pp.3-16.
- Bubakova, P., Pivokonsky, M. and Filip, P., 2013. Effect of shear rate on aggregate size and structure in the process of aggregation and at steady state. *Powder Technology*, *235*, pp.540-549.
- Carosso, P.A. and Pelizzetti, E., 1984. A stopped-flow technique in fast precipitation kinetics—the case of barium sulphate. *Journal of Crystal Growth*, 68(2), pp.532-536.
- Crowe, C.T., Troutt, T.R. and Chung, J.N., 1996. Numerical models for twophase turbulent flows. *Annual Review of Fluid Mechanics*, 28(1), pp.11-43.
- Debye, P. and Hückel, E., 1923. De la theorie des electrolytes. I. abaissement du point de congelation et phenomenes associes. *Physikalische Zeitschrift*, 24(9), pp.185-206.
- Dehkordi, A.M. and Vafaeimanesh, A., 2009. Synthesis of barium sulfate nanoparticles using a spinning disk reactor: effects of supersaturation, disk rotation speed, free ion ratio, and disk diameter. *Industrial & Engineering Chemistry Research*, 48(16), pp.7574-7580.

- Desmet, G., Verelst, H. and Baron, G.V., 1996. Local and global dispersion effects in Couette-Taylor flow—I. Description and modeling of the dispersion effects. *Chemical Engineering Science*, *51*(8), pp.1287-1298.
- DiPrima, R.C., Eagles, P.M. and Ng, B.S., 1984. The effect of radius ratio on the stability of Couette flow and Taylor vortex flow. *The Physics of fluids*, 27(10), pp.2403-2411.
- Dirksen, J.A. and Ring, T.A., 1991. Fundamentals of crystallization: kinetic effects on particle size distributions and morphology. *Chemical Engineering Science*, *46*(10), pp.2389-2427.
- Farahani, H.B., Shahrokhi, M. and Dehkordi, A.M., 2017. Experimental investigation and process intensification of barium sulfate nanoparticles synthesis via a new double coaxial spinning disks reactor. *Chemical Engineering and Processing: Process Intensification*, 115, pp.11-22.
- Fournier, M.C., Falk, L. and Villermaux, J., 1996. A new parallel competing reaction system for assessing micromixing efficiency—experimental approach. *Chemical Engineering Science*, 51(22), pp.5053-5064.
- Garside, J. and Jančić, S.J., 1976. Growth and dissolution of potash alum crystals in the subsieve size range. *AIChE Journal*, 22(5), pp.887-894.
- Haider, A. and Levenspiel, O., 1989. Drag coefficient and terminal velocity of spherical and nonspherical particles. *Powder Technology*, 58(1), pp.63-70.
- Haut, B., Amor, H.B., Coulon, L., Jacquet, A. and Halloin, V., 2003.
 Hydrodynamics and mass transfer in a Couette–Taylor bioreactor for the culture of animal cells. *Chemical Engineering Science*, 58(3-6), pp.777-784.
- Judat, B. and Kind, M., 2004. Morphology and internal structure of barium sulfate—derivation of a new growth mechanism. *Journal of Colloid and Interface Science*, 269(2), pp.341-353.

- Jung, W.M., Kang, S.H., Kim, W.S. and Choi, C.K., 2000. Particle morphology of calcium carbonate precipitated by gas–liquid reaction in a Couette– Taylor reactor. *Chemical Engineering Science*, 55(4), pp.733-747.
- KUBOI, R., KOMASAWA, I. and OTAKE, T., 1972. Behavior of dispersed particles in turbulent liquid flow. *Journal of Chemical Engineering of Japan*, 5(4), pp.349-355.
- Lewis, G.S. and Swinney, H.L., 1999. Velocity structure functions, scaling, and transitions in high-Reynolds-number Couette-Taylor flow. *Physical Review E*, 59(5), p.5457.
- Li, G., Yang, X. and Ye, H., 2015. CFD simulation of shear flow and mixing in a Taylor–Couette reactor with variable cross-section inner cylinders. *Powder Technology*, 280, pp.53-66.
- Li, J., Liu, D., Jiang, H., Wang, J., Jing, X., Chen, R., Zhu, W., Han, S., Li, W. and Wei, H., 2016. Effects of polyacrylic acid additive on barium sulfate particle morphology. *Materials Chemistry and Physics*, 175, pp.180-187.
- Mao, K.W. and Toor, H.L., 1970. A diffusion model for reactions with turbulent mixing. *AIChE Journal*, *16*(1), pp.49-52.
- Marchisio, D.L., Barresi, A.A. and Garbero, M., 2002. Nucleation, growth, and agglomeration in barium sulfate turbulent precipitation. *AIChE Journal*, *48*(9), pp.2039-2050.
- Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-rich hydroxide in reaction crystallization: Effect of Taylor vortex dimension and intensity. *Crystal Growth & Design*, *15*(4), pp.1726-1734.
- Nielsen, A.E., 1957. Nucleation in barium sulfate precipitation. *Acta Chemica Scandinavica*, *11*, pp.1512-1515.
- Nielsen, A.E., 1958. The kinetics of crystal growth in barium sulfate precipitation. *Acta Chemica Scandinavica*, *12*(5), pp.951-958.

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- Nielsen, A.E., 1959. The kinetics of crystal growth in barium sulfate precipitation. *Acta Chemica Scandinavica*, *13*, pp.1680-1686.
- Ottino, J.M., Ranz, W.E. and Macosko, C.W., 1979. A lamellar model for analysis of liquid-liquid mixing. *Chemical Engineering Science*, *34*(6), pp.877-890.
- Pagliolico, S., Marchisio, D. and Barresi, A.A., 1999. Influence of operating conditions on BaSO4 crystal size and morphology in a continuous Couette precipitator. *Journal of Thermal Analysis and Calorimetry*, 56(3), pp.1423-1433.
- Patel, C.M., Murthy, Z.V.P. and Chakraborty, M., 2012. Effects of operating parameters on the production of barium sulfate nanoparticles in stirred media mill. *Journal of Industrial and Engineering Chemistry*, 18(4), pp.1450-1457.
- Petrova, A., Hintz, W. and Tomas, J., 2008. Investigation of the precipitation of barium sulfate nanoparticles. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 31(4), pp.604-608.
- Phillips, R., Rohani, S. and Baldyga, J., 1999. Micromixing in a single-feed semi-batch precipitation process. *AIChE Journal*, *45*(1), pp.82-92.
- Soos, M., Wu, H. and Morbidelli, M., 2007. Taylor-Couette unit with a lobed inner cylinder cross section. *AIChE Journal*, *53*(5), pp.1109-1120.
- Takeda, Y., 1999. Quasi-periodic state and transition to turbulence in a rotating Couette system. *Journal of Fluid Mechanics*, 389, pp.81-99.
- Tai, C.Y. and Chen, P.C., 1995. Nucleation, agglomeration and crystal morphology of calcium carbonate. *AIChE Journal*, *41*(1), pp.68-77.
- Tai, C.Y. and Chen, F.B., 1998. Polymorphism of CaCO3, precipitated in a constant-composition environment. *AIChE Journal*, 44(8), pp.1790-1798.

- Thai, D.K., Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-rich hydroxide crystals in Taylor vortex flow. *Powder Technology*, 274, pp.5-13.
- Vicum, L., Mazzotti, M. and Baldyga, J., 2003. Applying a Thermodynamic Model to the Non-Stoichiometric Precipitation of Barium Sulfate. *Chemical Engineering & Technology*, 26(3), pp.325-333.
- Wereley, S.T. and Lueptow, R.M., 1998. Spatio-temporal character of nonwavy and wavy Taylor–Couette flow. *Journal of Fluid Mechanics*, *364*, pp.59-80.
- Wu, G., Zhou, H. and Zhu, S., 2007. Precipitation of barium sulfate nanoparticles via impinging streams. *Materials Letters*, *61*(1), pp.168-170.

CHAPTER 3

SHEAR CONTROLLABLE SYNTHESIS OF BARIUM SULFATE PARTCLES IN A TAYLOR-COUETTE FLOW REACTOR WITH VARIABLE CONFIGURATIONS OF INNER CYLINDER

SUMMARY

In Chapter 2, the interfacial phenomena in terms of the morphology transition of barium sulfate particles have been elaborated under the effect of the hydrodynamic characteristics. This Chapter concerns another particle property, particle size and its distribution. Also, a comparison between the classical TC reactor (CTC) and the lobed inner cylinder assembled TC reactor (LTC) was investigated through CFD modelling and experiments. The results have demonstrated that the Taylor vortices and turbulence induced shear rate distribution in the reactors have a significant influence on the final particle size distribution. The narrower shear rate distribution in the LTC is beneficial to the synthesis of particles with smaller size. The local turbulence intensification in the intra-Taylor vortices in the LTC effectively reduces the low shear strain regions. A strong correlation between the synthesized particle size and the local turbulent dissipation rate is existing. Shear induced by small turbulent eddies can inhibit particle growth. The LTC can be used for effectively shear controllable synthesis of particles.

3.1 Introduction

Reactive precipitation has been widely used to produce solid particles with various morphologies and sizes which play critical roles in evaluating the precipitates properties. Crystal precipitation is firstly induced by high supersaturation, involving nucleation, growth, agglomeration and breakup (Marchisio et al., 2006). During this process, mixing is of great importance as it can be seen as rate determining step involved in all processes due to the relatively rapid reaction rates of precipitation process and nucleation process (Judat et al., 2004). Intarasuwan et al. (2013) emphasized the important effect of mixing rate on the properties of zinc oxide powders. The reactive precipitation and the formation of particles take place at molecular scale, whose performance is mainly controlled by micromixing through the diffusion. However, macromixing that is characterized by the macro scale process determining the precipitation environment where micromixing occurs. Macromixing controlled by hydrodynamic characteristics can be also employed to enhance the mass transfer process. Therefore, the effect of mixing on particle quality is significantly important. This chapter aims to reveal the correlation between flow dynamics behaviour and initial solution conditions and to investigate their effects on barium sulfate particle size and its distribution.

The precipitation of barium sulfate has been studied using various types of chemical reactors with different configurations that can be used to realize certain hydrodynamic conditions. Petrova *et al.* (2008) synthesized barium sulfate particles by using a conventional stirred tank reactor, and obtained particles with size smaller than 100 nm. However, the aggregation occurred in this process was still able to lead the size to increase up to 5 μ m. Gradl *et al.*

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(2006) employed a T-mixer to prepare barium sulfate precipitates. They believed that this configuration can provide intensive mixing, beneficial to nanoparticle formation. Wu et al. (2007) used an impinging jet to produce barium sulfate in order to achieve good micromixing. Impinging stream was firstly proposed by Elperin (1961), then improved by Tamir (1994) and Botes (1998). The mixing characteristic size of this reactor spreads between several microns and several hundred microns, which leads to a shorter molecular diffusion length. Baldyga et al. (1995) had carried on a series of study about the reactive precipitation of barium sulfate particles to investigate the influence of operating conditions on crystals by employing a Rushton type stirred tank reactor. The result demonstrated that with increasing the stirred speed, the mean crystal size increases and eventually maintains at a maximum value. The authors suggested that the increase in stirring intensity could accelerate the diffusion of the reactants, which then results in the decrease of local supersaturation and nucleation rate, beneficial to the crystal growth into large particles. However, Tosun (1988) observed that the size of particles will approach a minimum with the increase of feed speed. The author suggested that this trend is caused by the combined effect of macromixing and micro-mixing on crystal nucleation and growth. An increase in the stirring speed enhances the local shear, consequently intensifying micro-mixing, beneficial to crystal nuclei growth. In addition, high stirring speed increases the rate of macromixing, reducing the concentration of reaction region and nucleation rate, resulting in particle growth becoming dominated. As a result, the increase of stirring speed may lead to the nonmonotonic variation of particle size.

TC reactor has been applied to many industrial applications in recent years due to its characteristics of shear controllable, narrow shear rate distribution and flexible mean residence time (Soos et al., 2007). Most of previous studies by applying TC reactor for synthesizing fine particles mainly focused on the effect of the hydrodynamics on particle formation process. Judat et al. (2004) employed a TC reactor, combined with external circulation pipe system by ensuring the flow to be turbulent, to study the effect of micromixing and macromixing on barium sulfate particle characteristics. They found that particle size decreases when applying a relatively high rotational speed of inner cylinder. Thus, they suggested that micromixing determines the synthesized particle size while macromixing controls the shape of crystals. This trend was observed in several other studies, such as, the works of Nguyen et al. (2012) and Marchisio et al. (2001). Also, Scargiali et al. (2009) discovered that a high axial flow rate leads to a smaller particle size. Aljishi et al. (2013) examined the effects of different flow structures on barium sulfate properties, in particular laminar flow and vortex flow at three different flow rates. They found that although the change of particle size are not clear when flow is laminar, however, vortices in different regions significantly affect the size and its distribution. Also, they conducted Lagrangian particle trajectory simulation to further interpret the results. Mayra and Kim (2015) studied the influence of Taylor vortices on the agglomeration process of precursor particles for lithium ion battery, demonstrating a decrease in particle size coupled with increase in turbulent shear rate. All the mentioned studies have indicated the hydrodynamic behaviour plays an important role in determining particle properties.

As the last chapter has dealt with the particle morphology transition under different hydrodynamic conditions, this chapter will mainly focus on particle size. As can be seen from the above mentioned literature, many studies only discussed the effect of stirred speed, only providing a qualitative trend of size change, but failed to interpret the their interrelationship. Therefore, in this chapter, such relationship will be realized by introducing correlation coefficient. Also, few studies have paid attention to the change of dominating factor at different levels of initial supersaturation. Additionally, although TC reactor can provide relatively homogeneous hydrodynamic environment in comparison to the conventional stirred tank, it has been revealed that there may exist weak shear regions close to the rotating cylindrical inner cylinder for the classical TC reactor, which may result in the mean residence time of the dispersed phase to be different from the carrier fluid in the process of particle preparation (Soos et al., 2007). Based on Soos et al.'s (2007) and Li et al.'s (2015) simulation, the inner cylinder with a lobed profile can effectively reduce low shear strain regions and further narrow the shear rate distribution. This chapter will adopt both classical TC reactor (CTC) and a modified TC reactor assemble with a rotating lobed geometry inner cylinder (LTC) to prepare barium sulfate particles, focusing on the influence of hydrodynamics on precipitation synthesis of barium sulfate particles. For this purpose, comparative studies by using the LTC to the CTC will be conducted experimentally together with the use of CFD modelling, focusing on the effects of the inner cylinder geometry, rotational speed, sampling time and initial supersaturation.

3.2 Experimental

3.2.1 Experimental setup

The schematic of experimental setup by employing the TC reactor with a volume of about 922 mL is illustrated in Figure 3.1 (a). Also, several photos are provided here to increase the understanding of the experiment procedures,

shown in Figure 3.1 (b). It has two coaxial cylinders. The aluminium alloy inner cylinder rotates while the plexiglass outer cylinder maintains static. Two shapes of inner cylinder adopted in the current study are the CTC and LTC mentioned in the introduction part. Figure 3.2 (a) shows the cross sectional profiles of both the CTC and LTC, and Figure 3.2 (b) presents the real inner cylinders adopted in experiment. The radiuses of inner and outer cylinders for the CTC are fixed at 40 mm and 50 mm, respectively, and the gap size is 10 mm. For the lobed geometry, the cross-section profile comprises three arcs with the identical radius but are connected by three mutual tangential lines. As the radius of the lobed inner cylinder is not constant, an equivalent radius can be estimated given by Equation (3.1) for the purpose of the comparison to the CTC. The dimensions of the CTC and LTC reactors are described in Table 3.1. The length of the both reactors was designed to 300 mm.

$$r_i = \frac{2A_i}{R_i} \tag{3.1}$$

where R_i is the perimeter, and A_i is the cross sectional area of the inner cylinder.





Figure 3.1 Schematic diagram for barium sulfate reactive precipitation in a TC reactor: (a) Experimental setup; and (b) Experimental procedures.



Figure 3.2 (a) Schematic of cross-section profiles for the CTC and LTC; (b) Inner cylinders used in experiment.

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Dimension	CTC	LTC
Radius of outer cylinder, r_o (mm)	50.00	50.00
Radius of inner cylinder, r_i (mm)	40.00	40.19

Gap size, <i>d</i> (mm)	10.00	9.81
Reactor length, L (mm)	300.00	300.00

3.2.2 Precipitation procedure

In the current experiments, two reactant solutions sodium sulfate (Na₂SO₄, analytical grade, Sinopharm Chemical Reagent Co., Ltd) and barium chloride (BaCl₂·2H₂O, analytical grade, Sinopharm Chemical Reagent Co., Ltd) were chosen to synthesize barium sulfate particles. All the experiments were conducted at the room temperature, 20 °C. Different series have been conducted by varying the rotational speed, sampling time and supersaturation.

Barium chloride solution was fed into the reactor at first to create an environment of excessive barium ions whilst the electrical double layer caused by these excessive barium ions can effectively maintain the suspension of barium sulfate particles in barium chloride solution (Eble, 2000). A servo motor was carefully calibrated in advance, and then used to control the rotational speed of the inner cylinder. Then, both solutions of barium chloride and sodium sulfate were fed into the reactor by using peristaltic pump with different feeding rates, ranging from 10 mL/min to 80 mL/min. Finally, the reaction was induced by local supersaturation. Based on the reactor volume and feeding rate, the average residence time t_{res} can be calculated for the given operation condition, where $t_{res} = \frac{v}{q}$ (V: the volume of the reactor; Q: the volumetric feeding rate). After the elapsing operation time is about one time of the average residence time, the suspension solution with the barium sulfate particles was continuously taken from the reactor for further treatment, such as washing, filtering and drying. From the trial experiments, the particle properties were measured for the

particles that were taken at different sampling times with the same feeding rate, and it has been affirmed that there is little impact of the sampling time on the synthesized particle sizes if the residence time has been obtained for the given operation condition because the reaction between barium chloride and sodium sulfate can be characterized by a fast reaction. Considering this fact, one third of the total suspension volume (i.e. 307 mL) was taken for each different operation condition from the reactor for analysis, i.e. the duration of sample collection is one third of the average residence time, defined as sampling time herewith.

Four main steps of a general precipitation (i.e. nucleation, growth, agglomeration and breakup) took place driven by supersaturation. The reaction between the two reactant solutions assuming instantaneous mixing obeys the following equation.

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + 2NaCl_{(aq)}$$
(3.2)

Supersaturation calculated by Equation (3.3) is the ratio of dissolved ion activity to its equilibrium solubility (Vicum *et al.*, 2003).

$$S = \frac{a}{a_{eq}} \approx \sqrt{\frac{c_{Ba^{2+}}c_{SO_4^{2-}}}{K_{SP}}}$$
(3.3)

where *a* is ion activity, and for a dilute solution, it can be replaced by ion molar concentration. K_{SP} is the solubility constant, which takes the value of 1.1×10^{-10} mol²/L² at 20 °C.

Nucleation rate can be estimated according to an empirical equation.

$$J = k_N S^n \tag{3.4}$$

where k_N is the nucleation coefficient, *and n* is the kinetic order. For current barium sulfate precipitation, k_N was assumed at 2.53×10^{39} m/s, and *n* is set to 15 (Baldyga *et al.*, 1995).

The total growth rate is defined as

$$B = k_g (S - 1)^2 (3.5)$$

where k_g is the growth coefficient, equal to 4×10^{-11} m/s at 20 °C.

The rotational speed is altered from 100 rpm to 1000 rpm in the experiments, and the sampling time ranges from 230 s to 1800 s. The effect of supersaturation was investigated by varying the initial reactants concentrations from 0.1 mol/L to 1.0 mol/L. Some of the experiments were carried out at least twice to ensure the repeatability of the results. During each experimental run, suspension products were continuously taken form the outlet, then washed by using deionized water at least three times. Finally, the products were filtered using filter paper, and dried in the oven at 100 °C for at least 24 hours.

X-ray diffraction (XRD, Bruker-AXS D8 advance powder diffractometer, Germany) analysis were conducted with Cu K α radiation source ($\lambda = 1.54056$ Å) to determine the structure and crystallite size of barium sulfate samples. The scanning angle was ranged from 10° to 90°. Particle morphology and microstructure were examined using SEM (Sigma VP, ZEISS, Germany).

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Particle size measurement was carried out through Malvern Mastersizer (Bettersize 2000, China), which works on dynamic light scattering (DLS) method. The measurement results of D50 were chosen to denote the average particle size in the following discussion.

3.3 Mathematical modelling

3.3.1 Governing equations

It has been realized that fluid shear behaviour is vital importance in affecting the process of reactive precipitation. In order to explore the relationship between rotational speed and particle size, CFD modelling was conducted to investigate the average shear rate and its distributions in the gap of the CTC and LTC. The effect of solid phase in current study can be neglected due to very low volume fraction of particles, i.e. one-way coupling being considered only. The governing equations for continuity and momentum can be solved by the simplified single phase model, which are described as follows,

Continuity equation:

$$\nabla \cdot \boldsymbol{u} = 0 \tag{3.6}$$

Momentum conservation equation:

$$\frac{\partial}{\partial t}(\rho \boldsymbol{u}) + \nabla \cdot (\rho \boldsymbol{u} \boldsymbol{u}) = -\nabla p + \nabla \tau + \rho \boldsymbol{g}$$
(3.7)

where ρ is the fluid density, \boldsymbol{u} is the instantaneous velocity, p is the static pressure, τ is the stress tensor (described below), and \boldsymbol{g} is the gravity. The stress tensor is written as

$$\tau = \mu[(\nabla \cdot \boldsymbol{u} + \nabla \cdot \boldsymbol{u}^T) - \frac{2}{3}(\nabla \cdot \boldsymbol{u})I]$$
(3.8)

where μ is the fluid dynamic viscosity.

Reynolds number can be used to classify the flow pattern developed in the TC reactor, defined by Equation (3.9).

$$Re = \frac{\omega_i r_i d}{\nu} \tag{3.9}$$

where ν is the kinematic viscosity of the suspension, and ω_i is the angular velocity of the inner cylinder. When the angular velocity of inner cylinder exceeds the critical Reynolds number, flow patterns transforms from circular Couette flow to Taylor vortex flow. Further increasing in the angular velocity will lead to the appearance of instabilities from wavy Taylor vortex flow (WVF) to turbulent Taylor vortex flow, and then fully developed turbulent Taylor flow.

For our case, the minimum rotational speed was set at 100 rpm, corresponding to the Reynolds number of 4157. Based on the classification of the flow pattern in the TC reactor, turbulent flow condition was achieved. Therefore, turbulence model can be used for equation closure. Soos *et al.* (2007) have compared the results of normalized shear rate distributions in the LTC using Reynolds stress model and standard k- ε model, respectively. They indicated that the differences were only marginal. Thus, the *k*- ε model was appropriate with low computational cost. However, the renormalization group k- ε model (RNG) was used because the flow in the TC reactor has the feature of very strong swirling and the effect of swirling on the turbulent shear stresses has to be accounted (Hanjalić, 1994).

The RNG k- ε are given by

$$\frac{\partial}{\partial t}(\rho k) + \nabla \cdot (\rho k \boldsymbol{u}) = \nabla \cdot \left(\frac{\mu_{eff}}{\sigma_k} \nabla k\right) + G_k - \rho \varepsilon$$
(3.10)

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\varepsilon \boldsymbol{u}) = \nabla \cdot \left(\frac{\mu_{eff}}{\sigma_{\varepsilon}}\nabla\varepsilon\right) + C_{1\varepsilon}\frac{\varepsilon}{k}G_{k} - C_{2\varepsilon}\rho\frac{\varepsilon^{2}}{k} - R_{\varepsilon} \qquad (3.11)$$

where G_k is the generation of turbulence kinetic energy resulting from the mean velocity gradients, given by

$$G_k = \mu_t (\nabla \boldsymbol{u} + \nabla \boldsymbol{u}^T) \nabla \cdot \boldsymbol{u}$$
(3.12)

 μ_{eff} is the effective viscosity, given by

$$\mu_{eff} = \mu + \mu_t \tag{3.13}$$

where μ_t is turbulent viscosity, evaluated as

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} \tag{3.14}$$

 R_{ε} is the extra strain rate term, given by

$$R_{\varepsilon} = \frac{C_{\mu}\rho\eta^{3}(1-\eta/\eta_{0})}{1+\beta\eta^{3}}\frac{\varepsilon^{2}}{k}$$
(3.15)

Other constants used in the RNG *k*- ε models are adopted as follows (Rahimi and Parvareh, 2005; Yakhot *et al.*, 1992; and Huang *et al.*, 2010): C_{μ} =0.0845, σ_{k} =0.0719, σ_{ε} =0.0719, $C_{1\varepsilon}$ =1.42, $C_{2\varepsilon}$ =1.68, β =0.012, η_{0} =4.38, $\eta = E \frac{k}{\varepsilon}$, $E^{2}=2E_{ij}E_{ij}$, E_{ij} =0.5($\nabla u + \nabla u^{T}$).

3.3.2 Numerical simulation approach

3D CFD simulation was carried out using commercial code FLUENT 17.0. The computational domain contains the gap between two concentric cylinders, and an inlet and an outlet zones. For the modelling of a non-circular inner cylinder, sliding mesh method was adopted. Thus, the computational domain was divided into an outer fluid zone and an inner fluid zone. The inner one involves the rotational lobed inner cylinder whose speed was set by mesh motion, while the outer zone was treated as stationary wall. Computational mesh was generated by ANSYS ICEM. The total cell number was set more than 1,100,000 with 147 nodes in the azimuthal direction, 480 nodes in the axial direction, and 16 nodes in the radial direction. In order to check mesh independence condition, the mesh in the radial direction was increased to 20 nodes, as the radial direction is crucial for the generation of Taylor vortex. Then, the wall shear stress on the surface of the inner cylinder was compared. The modelling results showed there was no significant difference. The standard wall function was set to ensure the value of y^+ for the wall boundary condition with log-law layer being ranged from 30 to 300. The surface of the lobed inner cylinder was set as moving wall, which was static relative to adjacent cell zone. The solution inlet and the product outlet were set as velocity inlet and pressure outlet respectively. The convergence criterion was set at 1×10^{-3} for all parameters between two successive iterations, and the time step of 0.001 s was chosen for the temporal discretization. The pressure-velocity coupling was realized by SIMPLEC algorithm.

3.4 Results and discussion

3.4.1 Effect of inner cylinder geometry at different rotational speeds on particle size and distribution

The effect of inner cylinder geometry on particle size was investigated at different shear strain rates, characterized by using different rotational speeds from 100 rpm to 1000 rpm. Figure 3.3 illustrates the SEM images of particles precipitated in the CTC and LTC respectively. Particles in each reactor show a transition from irregular big flakes with large size to spherical particles with small size when increasing the rotational speed, as shown in Figure 3.4 (solid lines). Final particles can be seen as products of the agglomeration of crystallites, while crystallites are composed of thousands of unit cells stacked in a three dimension matrix. Therefore, each crystallite has its particular Miller indices (h k l). In order to ensure the crystallite structure and phase composition of barium sulfate particles, XRD results are shown in Figure 3.5. The observed peaks in Figure 3.5 (JCPDS Card Files No. 24-1035) reveal that pure barium sulfate particles with a typical orthorhombic structure have been synthesized in experiment. The high intensity of planes (021), (210), (121), (140) and (212) reveals the orientation of crystal growth. Although many planes exist in a typical BaSO₄ crystal, crystal growth has some preferred directions. Moreover, the relative intensity of planes (140) and (212) is weaken in the LTC, indicating a

relatively fast crystal growth along the other three planes. Such growth orientation could be beneficial for further crystal agglomeration to form final particles. The average crystallite sizes were estimated according to Scherrer equation

$$D = \frac{\kappa\lambda}{\delta\cos\theta} \tag{3.16}$$

where K is the constant shape factor, which is 0.9 (Nagaraja *et al.*, 2007), λ is the wavelength of X-ray radiation, which is 0.145056 nm, δ is the peak width at half minimum height, and θ is diffraction angle. Three typical crystallite planes (0 2 1), (2 1 0), and (1 2 1) were chosen to calculate the average crystallite size. Figure 3.4 (dash lines) shows the results of the change of crystallite size at different rotational speeds, which decreases slightly with the increase of rotational speed. However, as can be seen from the solid lines in Figure 3.4, the change of particle size is ranged from 100 nm to 800 nm, thus a relatively narrow range of crystallite size from 50 nm to 70 nm can be neglected. This suggests that flow dynamics has negligible effect on the nature of crystallization kinetics, but significantly affects crystallite growth and agglomeration. Without the impact of turbulence induced shear, particles are likely formed from a single core, as observed in the study of Mao and Huang (2007). They suggested that with the increase of the malic acid concentration, the morphology of CaCO₃ transformed from a single block to aggregate growing from a single core. However, a strong turbulence involved in this study leads to a different result. It can be seen from Figure 3.3, the marked area indicates the agglomeration of particles. This can be deduced from the comparison of time scale. The characteristic induction time for the generation of nuclei is extremely short, which is about 1×10^{-3} s, and the nucleation rate is very fast (~1×10¹³

nucleus/m²s). Micromixing time can be evaluated from eddy engulfment model, presented by Baldyga and Bourne (1984)

$$t_m = \frac{12}{\ln 2} \sqrt{\frac{\nu}{\varepsilon}} \tag{3.17}$$

The average micromixing time is the order of 10^{-2} s, which is larger than nucleation time scale. Furthermore, the length scale of the smallest eddies is assumed to be proportional to Kolmogorov length scale, defined by

$$l_{edd} = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4} \tag{3.18}$$

The eddy length scale is the order of 10⁻⁵ m. As it has been mentioned before, the stack of these crystallites forms final particles, while eddies have a larger scale than crystallites. This means that eddy shear cannot influence nucleation process. However, it can affect the interactions such as agglomeration among these crystallites, and then eddies work on final particle size through entrapment. Stokes number can be used to determine particle entrapment by eddies, defined by

$$St = \frac{\rho_p d_p^{-2} u_t}{18\mu l_{eddy}} \tag{3.19}$$

where ρ_p is the particle density, d_p is the particle size, and u_t is the terminal velocity of particles. For current case, the Stokes number is the order of 10⁻⁴, which is much smaller than 1 (*St*<<1.0), indicating the occurrence of particle trapping. Therefore, from the results of SEM, XRD and flow field time and

length scales, it is suggested that although final particle size changes with flow field, flow dynamics has little effect on crystallite formation process.



Figure 3.3 SEM images of barium sulfate particles precipitated in the: (a) CTC; and (b) LTC, at different inner cylinder rotational speeds: $\omega_i = (i) 100$; (ii) 300; (iii) 600; (iv) 800; (v) 1000 rpm.



Figure 3.4 Particle size and crystallite size at different rotational speeds in the CTC and LTC.



(a)



Figure 3.5 XRD results of crystallites in the: (a) CTC; and (b) LTC.

Variation of micromixing time at different rotational speeds is illustrated in Figure 3.6 for both the CTC and LTC. The reduction of particle size with increased rotational speed can be attributed to the fact that a high rotational speed strengthens micromixing efficiency. From the experimental results of Judat *et al.* (2004), they also observed a reduction trend of particle size when increasing the cylinder rotational speed. As indicated by Aljishi *et al.* (2013), the increase of micromixing rate could result in a rather high local supersaturation, then a small particle size can be formed. Because nucleation is extremely sensitive to supersaturation, and the improvement of nucleation step can facilitate the creation of small particles. This will be elaborated in Section 3.4.3.

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Figure 3.6 Micromixing time at different rotational speeds in the CTC and LTC.

Also, the sizes of particles that are synthesized using the CTC at any rotational speed from 100 rpm to 1000 rpm are larger than those synthesized using the LTC. In order to interpret this phenomenon, the radial velocity field in vertical y-z cutting planes at different rotational speeds was examined as shown in Figure 3.7. It can be seen that the size of each pair of Taylor vortices in the LTC has changed in the circumferential direction, from the larger gap to smaller gap as compared to the CTC, where there is no significant changes along the circumferential direction. Such change significantly affects shear distribution in the vortices. In the region between two counterpart toroidal vortices, the fluid flow can be considered as either radially outward or inward impinging jet flows, as marked in Figure 3.7 (e). The outward velocities of the jet regions in the LTC at the largest gap for a given rotational speed are higher than those in the CTC at the largest gap region of the LTC. This shear turbulence intensified regions correspond to a high shear gradient and a high turbulence generation, thus

indicating the local shear especially for $G = \sqrt{\frac{\varepsilon}{\nu}}$. Figure 3.8 illustrates the time average shear stain rate on the vertical plane, which is defined as by

$$\gamma = \sqrt{\frac{1}{2}\Delta_{ij}\Delta_{ij}}, \qquad \Delta_{ij} = \left(\frac{\partial \bar{u}_i}{\partial x_j} + \frac{\partial \bar{u}_j}{\partial x_i}\right) \tag{3.20}$$

where *i* is direction indicator. As shown in Figure 3.8, the highest shear strain rate is formed in the jet regions, while the lowest shear strain rate presents in the core of the vortices. In order to quantitatively identify the influence of geometry on shear strain rate, its distribution is shown in Figure 3.9 at different rotational speeds. It can be seen that there exists two obvious secondary peaks for the CTC, indicating a non-uniform distribution of shear strain rate. This might lead to a wide spread of particle size when using the CTC, as can be seen from Figure 3.10. This observation is consistent with the distributions of the shear strain rate for both the CTC and LTC. Though the average turbulent shear is enhanced as the result of the increased rotational speed of the inner cylinder, more turbulent eddies with high frequency may generate with the occurrence of secondary peak on the shear strain rate distribution, thus giving a slight broad spread of particle size distribution for case of the CTC.



(CTC) (LTC)

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Figure 3.7 Radial velocity distributions in the vertically cutting plane of the TC reactor working at different rotational speeds, left for the CTC and right for the LTC: (a) $\omega_i = 100$ rpm; (b) $\omega_i = 300$ rpm; (c) $\omega_i = 600$ rpm; (d) $\omega_i = 800$ rpm; (e) $\omega_i = 1000$ rpm.



Figure 3.8 Shear strain rate in the vertically cutting plane of the TC reactor working at different rotational speeds, left for the CTC and right for the LTC: (a) $\omega_i = 100$ rpm; (b) $\omega_i = 300$ rpm; (c) $\omega_i = 600$ rpm; (d) $\omega_i = 800$ rpm; (e) $\omega_i = 1000$ rpm



Figure 3.9 Distribution of the normalized shear strain rate on the cross section at different rotational speeds in the CTC and LTC: (a) $\omega_i = 100$ rpm; (b) $\omega_i =$ 300 rpm; (c) $\omega_i = 600$ rpm; (d) $\omega_i = 800$ rpm; (e) $\omega_i = 1000$ rpm.



Figure 3.10 Particle size distribution at different rotational speeds in the CTC and LTC: (a) $\omega_i = 100$ rpm; (b) $\omega_i = 300$ rpm; (c) $\omega_i = 600$ rpm; (d) $\omega_i = 800$ rpm; (e) $\omega_i = 1000$ rpm.
As can be seen from Figures 3.4 and 3.6, it is also worth noticing that with the increase of rotational speed, the difference in micromixing time between two reactors becomes small, consequently resulting in the similar trend of particle size distribution for both the CTC and LTC. It can be deduced that there exists a critical balance point between turbulent shear dispersion of reactant solution and particle entrapment by turbulent eddies. After reaching this critical point, particle agglomeration and turbulent shear attains an equilibrium, i.e. the particle size growth via agglomeration will be significantly controlled by the local turbulent shear caused by smaller turbulent eddies. The effect of turbulent eddies on particle agglomeration can be realized by using population balance model (PBM), which is underway based on currently available experimental data.

3.4.2 Effect of sampling time on particle size in the LTC reactor

Due to the intensification effect by using the lobed inner cylinder geometry, the following experimental results were obtained based on the LTC from 300 rpm to assess the effect of sampling time on particle size, as the intensified effect at 100 rpm is not remarkable. The effect of sampling time was examined by varying sampling time, ranging from 230 s to 1800 s, corresponding to the duration of sample continuously collected from the reactor, shown in Figure 3.11 (a). The results show a complex dependence. Generally speaking, particle size firstly reduces, and then increases with increasing the sampling time. As shown in Figure 3.11 (a), with the increase of rotational speed, the transition point for minimum particle size appears in a rather short sampling time. This may be attributed to the superposition of a small axial flow to the original Taylor vortices formed in the reactor. It has been suggested that the addition of an axial

flow will result in the delayed presence of critical Reynolds number (Snyder, 1962). Because the increase in axial flow can diminish the dominance of centrifugal force, then macromixing efficiency will be improved. A long sampling time facilitates the overall macromixing on reactor scale. After transition point, the increase of particle size may be likely attributed to a rather long time for crystallites collision so that particle agglomeration is facilitated. More crystallites stack in the local environment, forming particles with large size. However, particle size maintains almost unchanged as the consequence of turbulent eddy shear control. Turbulent eddy is capable to lead to a better macro dispersion of the reactant solution and uniform distribution of the reactive mass. A well distributed reactant can reduce the accumulation of local mass, inhibiting particle growth. Thus, the flow shear generated inside the reactor mainly promotes the solution dispersion and particle agglomeration to affect final particle size. For the purpose of illustrate the effect of turbulent shear controlled by turbulence dissipation rate on the particle size, a correlation between the volumetric average turbulent dissipation rate and particle size is defined by a correlation coefficient R_{ave} as follows:

$$R_{ave} = \frac{\overline{\varepsilon}_{i'} \overline{d}_{p_i}}{\frac{1}{N} \sum_{i=1}^{N} \overline{\varepsilon}_{i'} \overline{d}_{p_i}}$$
(3.21)

where *i* denotes different rotational speeds. The time averaging dissipation rate was taken from the CFD results at different rotational speeds, and the particle size was the average value of the various sampling times. From Figure 3.11 (b), it can be seen that the correlation between fluid dissipation rate and particle size is enhanced with the increase of rotational speed. More specifically, in order to involve the effect of sampling time in this correlation, another more precise correlation coefficient R(t) is suggested as follows:

$$R(t) = \frac{\overline{\overline{\varepsilon} \cdot \overline{d}_p(t + \Delta t)}}{\sqrt{\overline{\varepsilon}^2} \cdot \sqrt{\overline{d}_p(t)^2}}$$
(3.22)

In the Equation (3.22), Δt is the time interval of sampling, and the particle size at the initial sampling time was chosen as reference point. Figure 3.11 (c) shows the results of the correlation between the turbulent dissipation rate and particle size with the increase of sampling time. It can be seen that a small rotational speed of 300 rpm has a reduced trend of correlation. However, at the other three rotational speeds, correlation coefficients asymptotically approach a constant after a reduction. Moreover, strong correlations (R > 1) are observed at 600 rpm and 800 rpm. This may indicate that turbulent dissipation rate has a significant effect on the particle size at 600 rpm and 800 rpm as the local shear due to the turbulent eddies may strongly interact with the particles. Also, this effect will be lagged over successive time intervals. When the value of correlation levels off, the extension of sampling time has little effect on particle size. This result can serve as references in the field of particle preparation in order to obtain the desired particle size.





Figure 3.11 Particle size and correlation at different sampling times in the LTC: (a) Particle size; (b) Average correlation coefficient between turbulent dissipation rate and particle size; and (c) Correlation coefficient at different sampling times.

3.4.3 Effect of initial supersaturation on particle size in the LTC

Rotational speed and the feeding rate was fixed at 1000 rpm to investigate the effect of supersaturation. All five runs were based on stoichiometric reaction of barium ion and sulfate ion, which were 0.1 mol/L, 0.2 mol/L, 0.5 mol/L, 0.8 mol/L and 1.0 mol/L respectively. Figure 3.12 shows the variation of particle size, which decreases firstly and then rises slightly until a constant value with the increase of supersaturation. Many studies have indicated a continuous reduction trend of particle size with the increase of supersaturation (Dehkordi and Vafaeimanesh, 2009; Barresi *et al.*, 1999; and Garside and Shah, 1980). It is obvious from the kinetics of nucleation and growth, demonstrated in the Equations (3.4) and (3.5) respectively, the rate order of nucleation is higher than that of growth, thus nucleation process will be enhanced stronger when increasing supersaturation. It has been suggested by many studies (Kucher *et al.*, 2006; McCarthy *et al.*, 2007; and Takiyama, 2012), the increase of nucleation

rate will facilitate the generation of a large amount of nuclei, and then small particles can be formed. However, particle size is found not to be continuously reduced in our experiment. After increasing the concentration to exceed 0.5 mol/L, i.e., supersaturation being greater than 8214, particle size increases slightly. This is very likely caused by two aspects, one is particle growth and the other one is force balance. Firstly, particle growth always exists. At a high concentration, the available reactant around the surface of crystallites is sufficient. Besides nucleation, a large amount of reactant is used for particle growth locally. Secondly, high concentration increases the fluid kinematic viscosity. The kinematic viscosity at the highest concentration of 1.0 mol/L was approximately 0.85 times higher than that at 0.1 mol/L. As indicated in Equation (3.9), Reynolds number, which determines flow pattern and turbulence degree is inversely proportional to the kinematic viscosity. Thus, the increase of kinematic viscosity at a high concentration will reduce turbulence. Accordingly, the external fluid shear force is weaken. However, based on the empirical relation proposed by Brunsteiner et al. (2005), agglomeration is strengthened at high supersaturation. Therefore, the internal cohesive force is dominant, which facilitates particles to agglomerate into large size. Thus, the overall effect of both above mentioned aspects causes a slight increase of particle size.



Figure 3.12 Variation of particle size at different initial supersaturation ratios in the LTC.

3.5 Conclusions

The present study employed a modified TC reactor assembled with a novel lobed inner cylinder to produce barium sulfate particles at different operating conditions. Compared with the CTC, the use of the LTC can effectively improve the process of reactive precipitation through changing the turbulence induced shear strain rate distribution in the inwards and outwards impinging jet regions of Taylor vortices, which has the potential for the formation of small particles. The variation of the gap between the outer cylinder and lobed inner cylinder in the LTC deforms the embedded Taylor vortices and leads to the local turbulence intensification. It is also revealed with the LTC that when working at a high rotational speed, adoption of a relatively long sampling time and high supersaturation is able to reliably produce small particles. The conclusions reached from the present study are as follows:

(1) There exists a strong correlation between the synthesized particle size and the local turbulent dissipation rate. Also, the shear induced by small turbulent eddies can inhibit particle growth;

(2) The effect of the supersaturation on particle size is non-monotonic, which is likely to attribute to the impact of turbulent eddies induced shear on particle agglomeration, which needs to be investigated further. The results have suggested that it is realizable for shear controllable synthesis and production of particles. The LTC is one of such reactors which can be used for effectively shear controllable synthesis.

References

- Aljishi, M.F., Ruo, A.C., Park, J.H., Nasser, B., Kim, W.S. and Joo, Y.L., 2013. Effect of flow structure at the onset of instability on barium sulfate precipitation in Taylor–Couette crystallizers. *Journal of Crystal Growth*, 373, pp.20-31.
- Baldyga, J. and Bourne, J.R., 1984. A Fluid Mechanical Approach to Turbulent Mixing and Chemical Reaction Part III Computational and Experimental Results for the New Micromixing Model. *Chemical Engineering Communications*, 28(4-6), pp.259-281.
- Baldyga, J., Podgorska, W. and Pohorecki, R., 1995. Mixing-precipitation model with application to double feed semibatch precipitation. *Chemical Engineering Science*, 50(8), pp.1281-1300.
- Barresi, A.A., Marchisio, D. and Baldi, G., 1999. On the role of micro-and mesomixing in a continuous Couette-type precipitator. *Chemical Engineering Science*, 54(13-14), pp.2339-2349.
- Botes, F. G., Lorenzen, L., and Van Deventer, J. S. J., 1998. The development of high intensity gas-liquid jet reactors. *Chemical Engineering Communications*, 170(1), 217-244.
- Brunsteiner, M., Jones, A.G., Pratola, F., Price, S.L. and Simons, S.J., 2005. Toward a molecular understanding of crystal agglomeration. *Crystal Growth & Design*, 5(1), pp.3-16.
- Dehkordi, A.M. and Vafaeimanesh, A., 2009. Synthesis of barium sulfate nanoparticles using a spinning disk reactor: effects of supersaturation, disk rotation speed, free ion ratio, and disk diameter. *Industrial & Engineering Chemistry Research*, 48(16), pp.7574-7580.

- Eble, A., 2000. Precipitation of nanoscale crystals with particular reference to interfacial energy. *PhD thesis, Technische Universitat Munchen*, Munchen.
- Elperin, I. T., 1961. Heat and mass transfer in opposing currents. *Journal of Engineering Physics*, 6, 62-68.
- Garside, J. and Shah, M.B., 1980. Crystallization kinetics from MSMPR crystallizers. *Industrial & Engineering Chemistry Process Design and Development*, 19(4), pp.509-514.
- Gradl, J., Schwarzer, H.C., Schwertfirm, F., Manhart, M. and Peukert, W., 2006.
 Precipitation of nanoparticles in a T-mixer: coupling the particle population dynamics with hydrodynamics through direct numerical simulation. *Chemical Engineering and Processing: Process Intensification*, 45(10), pp.908-916.
- Hanjalić, K., 1994. Advanced turbulence closure models: a view of current status and future prospects. *International Journal of Heat and Fluid Flow*, 15(3), pp.178-203.
- Huang, Q., Yang, C., Yu, G. and Mao, Z.S., 2010. CFD simulation of hydrodynamics and mass transfer in an internal airlift loop reactor using a steady two-fluid model. *Chemical Engineering Science*, 65(20), pp.5527-5536.
- Intarasuwan, K., Amornpitoksuk, P. and Suwanboon, S., 2013. Effect of the mixing rate on the morphology and photocatalytic activity of ZnO powders prepared by a precipitation method. *Advanced Powder Technology*, 24(6), pp.999-1005.
- Judat, B. and Kind, M., 2004. Morphology and internal structure of barium sulfate—derivation of a new growth mechanism. *Journal of Colloid and Interface Science*, 269(2), pp.341-353.

- Judat, B., Racina, A. and Kind, M., 2004. Macro-and Micromixing in a Taylor-Couette Reactor with Axial Flow and their Influence on the Precipitation of Barium Sulfate. *Chemical Engineering & Technology*, 27(3), pp.287-292.
- Kucher, M., Babic, D., & Kind, M. (2006). Precipitation of barium sulfate: experimental investigation about the influence of supersaturation and free lattice ion ratio on particle formation. *Chemical Engineering and Processing: Process Intensification*, 45(10), pp.900-907.
- Li, G., Yang, X. and Ye, H., 2015. CFD simulation of shear flow and mixing in a Taylor–Couette reactor with variable cross-section inner cylinders. *Powder Technology*, 280, pp.53-66.
- Mao, Z., & Huang, J. (2007). Habit modification of calcium carbonate in the presence of malic acid. *Journal of Solid State Chemistry*, 180(2), pp.453-460.
- Marchisio, D.L., Barresi, A.A. and Fox, R.O., 2001. Simulation of turbulent precipitation in a semi-batch Taylor-Couette reactor using CFD. *AIChE Journal*, *47*(3), pp.664-676.
- Marchisio, D.L., Rivautella, L. and Barresi, A.A., 2006. Design and scale-up of chemical reactors for nanoparticle precipitation. *AIChE Journal*, 52(5), pp.1877-1887.
- Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-Rich hydroxide in reaction crystallization: Effect of Taylor vortex dimension and intensity. *Crystal Growth & Design*, 15(4), pp.1726-1734.
- McCarthy, E. D., Dunk, W. A. E., & Boodhoo, K. V. K. (2007). Application of an intensified narrow channel reactor to the aqueous phase precipitation of barium sulphate. *Journal of Colloid and Interface Science*, 305(1), pp.72-87.

- Nagaraja, B. M., Abimanyu, H., Jung, K. D., & Yoo, K. S., 2007. Preparation of mesostructured barium sulfate with high surface area by dispersion method and its characterization. *Journal of Colloid and Interface Science*, 316(2), pp.645-651.
- Nguyen, A.T., Joo, Y.L. and Kim, W.S., 2012. Multiple feeding strategy for phase transformation of GMP in continuous Couette–Taylor crystallizer. *Crystal Growth & Design*, *12*(6), pp.2780-2788.
- Petrova, A., Hintz, W. and Tomas, J., 2008. Investigation of the precipitation of barium sulfate nanoparticles. *Chemical Engineering & Technology*, 31(4), pp.604-608.
- Rahimi, M., Parvareh, A., 2005. Experimental and CFD investigation on mixing by a jet in a semi-industrial stirred tank. *Chemical Engineering Journal*, 115(1-2), pp. 85–92.
- Snyder, H.A., 1962, January. Experiments on the stability of spiral flow at low axial Reynolds numbers. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 265(1321), pp.198-214.
- Soos, M., Wu, H. and Morbidelli, M., 2007. Taylor-Couette unit with a lobed inner cylinder cross section. *AIChE Journal*, *53*(5), pp.1109-1120.
- Takiyama, H. (2012). Supersaturation operation for quality control of crystalline particles in solution crystallization. Advanced Powder Technology, 23(3), pp.273-278.
- Tamir, A., 1994. Impinging-Stream Reactors Fundamentals and Applications, Elsevier Science, Amsterdam.
- Tosun, G., 1988, May. An experimental study of the effect of mixing on the particle size distribution in BaSO4 precipitation reaction. In *Proceedings* of the 6th European Conference on Mixing (p.161). Cranfield, England: BHRA

- Vicum, L., Mazzotti, M., & Baldyga, J., 2003. Applying a thermodynamic model to the non-stoichiometric precipitation of barium sulfate. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*, 26(3), pp.325-333.
- Wu, G., Zhou, H. and Zhu, S., 2007. Precipitation of barium sulfate nanoparticles via impinging streams. *Materials Letters*, *61*(1), pp.168-170.
- Yakhot, V., Orszag, S.A., Thangam, S., Gatski, T.B., Speziale, C.G., 1992. Development turbulence models for shear flow by a double expansion technique. Physics of Fluids A 4, 1510–1520.

CHAPTER 4

EFFECT OF HYDRODYNAMIC HETEROGENEITY ON MICROMIXING INTENSIFICATION IN A TAYLOR-COUETTE FLOW REACTOR WITH VARIABLE CONFIGURATIONS OF INNER CYLINDER

SUMMARY

In previous chapters, hydrodynamics has been confirmed to play an important role in determining barium sulfate particle properties. However, the fundamental study of hydrodynamic mechanism has not been investigated. As chemical reaction takes place at the molecular level, mixing at the similar scale can directly influence its course. Thus, the effect of hydrodynamic heterogeneity on micromixing intensification in both the CTC and LTC has been investigated by adoption of a parallel competing iodide-iodate reaction system, focusing on the effects of the Reynolds number of the TC reactor, the acid concentration, and the feeding time on the micromixing behaviour. The Segregation index (Xs) was employed as an indicator to evaluate the micromixing efficiency. It is revealed in general that Xs decreases with the increase of Reynolds number and feeding time but increases with the increase of acid concentration for both the CTC and LTC. However, the LTC does present

a better micromixing performance at various operating conditions compared with that of the CTC as affirmed by both the experimental and CFD simulation results. It is found that the local turbulence intensity in the outward and the inward impinging jet flows induced by turbulent Taylor vortices is remarkably enhanced due to alteration of the configuration of the inner cylinder from a circular cross-sectional profile to the lobed profile. Based on the incorporation model, the minimum micromixing time in both reactors was estimated to be of the order of 10^{-5} s, which is much smaller than that of the conventional stirred tank reactor (2×10⁻³ to 2×10⁻² s).

4.1 Introduction

During the synthesis of various micro/nano particles, the hydrodynamics of the mixing in the reactors has been recognised as playing a determinant role in determining the synthesised particle properties. In particular, micromixing, which takes place at the molecular scale, has been considered as the rate determining step during chemical reaction of particle crystal growth in the reactors, especially for the fast chemical reactions involved as pointed out by Baldyga and Bourne (1999). A perfect micromixing condition can effectively increase the yield of the desired particle and reduce by-products in the synthesis process at the same time. It should be mentioned that even mixing is deemed to be effective at the macro scale, it may not have achieved homogeneity at the

micro scale yet. Thus, the improvement of micromixing will be beneficial to the intensification of the particle synthesis process.

Various kinds of reactor have been developed and investigated in previous studies, aiming to improve the mixing performance. For example, the use of a spinning disk reactor (Jacobsen and Hinrichsen, 2012), impinging jet reactor (Liu et al., 2014), microchannel reactor (Shi et al., 2012), T-shaped reactor (Gao et al., 2015), and high shear mixer (Qin et al., 2017) have all been studied before. TC reactor with the features of controllable mean residence time and narrow shear rate distribution has also received a lot of attention. This type of reactor has a simple configuration, where the inner cylinder rotates relative to the outer one. Jung et al. (2000) prepared calcium carbonate particles by a gas-liquid reaction system using a TC reactor, and obtained three particle morphologies (cube-like, transition and spindle). They attempted to introduce an enhancement factor correlated with the mass transfer rate, and suggested that the particle shape change is dependent on this enhancement factor. Tang et al. (2019) have investigated the morphology change of copper sulfide nanoparticles by using such reactor and they have also found that an intensified mass transfer rate can be achieved using the TC reactor. By tracing the other applications, Haut *et al.* (2003) employed a TC device to culture animal cells and found that the device is more appropriate than a conventional stirred tank in terms of the control of oxygen content and cell suspension. They believed that the adoption of TC reactor can effectively enhance mass transfer rate and create a relatively mild

environment for cell growth. Kim and his co-researchers have employed the TC reactor to synthesise many types of fine particles, such as cathode precursors for lithium ion batteries (Mayra and Kim, 2015; Thai *et al.*, 2015; and Kim and Kim, 2017), barium sulfate (Aljishi *et al.*, 2013), L-histidine (Park and Kim, 2018), and Guanosine 5-monophosphate (Nguyen *et al.*, 2011). Their work mainly focused on the applications of the TC reactor during various particle production processes. However, these studies lacked the fundamental investigation of the mechanisms involved behind the mixing, mass transfer and heat transfer processes.

During particle synthesis process, many previous studies have indicated that even a minor change of reactor configuration will lead to a significant effect on the micromixing performance. Jacobsen and Hinrichsen (2012) investigated the micromixing characteristics in a spinning disk reactor with different feeding locations and surface structures. In addition, by validation, they synthesised barium sulfate particles with different reactor configurations and obtained various particle morphologies and sizes. Bertrand *et al.* (2016) applied CFD to simulate the micromixing in three types of mixers from the same family but with some geometrical differences: T-shaped tube, Y-shaped tube, and Hartridge-Roughton mixing device. Both experimental and numerical results indicated that the Hartridge-Roughton tube is the most efficient one. Zhu *et al.* (2019) synthesised cathode precursor $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ for lithium ion batteries in a stirred tank with four different types of impeller. They finally

obtained particles with different shapes and tap densities and consequently, different electrochemical performances. They attributed these differences to the different flow fields generated by four impellers. All these previous studies have revealed that geometrical optimisation is an effective and economical approach to improve the performance of these existing reactors. As mentioned earlier, TC reactor has many features that are beneficial to the particle synthesis due to the fast mass transfer and easy shear control. However, the shear regions in the TC reactor are not locally uniformly distributed. In order to better utilise the advantage of overall shear control, the modification of the classical TC reactor may improve the features of local turbulent shear. Soos et al. (2007) proposed a lobed profile for the inner cylinder in order to reduce the low velocity gradient region. They found that this configuration can successfully enhance the local shear rate in the vicinity of the inner cylinder. Li et al. (2015) have compared the mixing performance in the TC reactor with various cross-sectional profiles of inner cylinder including a lobed one using CFD simulation in terms of flow patterns, shear strain rate distribution and micromixing time. They ascertained that the mixing performance improves when using the inner cylinder with a lobed profile. Liu et al. (2020) have reported the synthesis of the barium sulfate particles by using the TC reactor with the classical circular cross-sectional profile inner cylinder and a lobed profile inner cylinder. The experimental results clearly indicate that the properties of the secondary particles are different in terms of particle morphology, particle size and size distribution. The aforementioned investigations have implications where the mixing in the TC

reactor is significantly affected by the hydrodynamics in the reactor and also by the inner cylinder configuration adopted.

So far, the micromixing process in the TC reactor has not been clearly understood though a number of experimental work and theoretical studies conducted (Drozdov, 2002; Racina and Kind, 2006; and Richter et al., 2008). Also, these previous studies have mainly focused on the TC reactors with the circular cross-sectional profile inner cylinder and the modifications on the configuration were mainly subjected to the changes of gap size and aspect ratio (DiPrima, 1984; Xiao et al., 2002). The impact of configuration variation on the micromixing performance, especially the inner cylinder alteration, is still rarely studied in the literature. Richter et al. (2009) compared mixing performance of the classical TC reactor and a novel TC reactor with ribbed rotor assembled in laminar flows with Reynolds numbers smaller than 2.0. In order to test the micromixing performance down to the molecular level, they adopted alkaline saponification of ethylacetate as the reactive system. It is found that ribbed configuration can segregate reactant flows, leading to backmixing. Thus, the authors indicated that configuration modification can be seen as a promising method for process intensification. Similarly, Li et al. (2015) also suggested that as chemical reactions take place at a molecular level, micromixing may dominate this process. In their work, micromixing time was estimated in the TC reactors by $t_m = \frac{12}{\ln 2} \sqrt{\frac{\nu}{\epsilon}}$ with five different inner cylinders including a lobed one, where ε is the turbulent kinetic energy dissipation rate, obtained from CFD

modelling results. Compared to the classical TC reactor, the lobed TC reactor shows a rather small micromixing time. Their work mainly focused on CFD modelling technique applied to the TC reactor system, while lacking experimental data to calculate micromixing time.

The aim of this chapter is to investigate the micromixing performance in the TC reactor with two different types of inner cylinders and to obtain the guidelines for further enhancing micromixing performance through the configuration modification. A parallel competing system based on the iodide-iodate reaction proposed by Villermaux and co-workers (Villermaux et al., 1994; Fournier et al., 1996) has been employed, attempting to reveal the effects of key operating parameters on the segregation index, which can reasonably serve as an indicator for assessing the micromixing performance. The key parameters include the Reynolds number based on the gap size, the reactant feeding time and the acid concentration. In addition, the micromixing time based on the experimental data by employing the incorporation model are also evaluated and compared. This chapter will be organised as follows. Section 4.2 will present the theoretical background and modelling details for evaluating the micromixing using the iodide-iodate reaction system, while Section 4.3 will present the experimental details for such chemical probe in the TC reactor with micromixing performance evaluation. Section 4.4 will present the results and discussion and finally, Section 4.5 will summarise the conclusions derived from the study.

4.2 Micromixing characterization modelling

Various chemical reaction schemes serving as molecular probes have been proposed and commonly accepted by researchers to characterise the micromixing performance for the reaction system involved. Typical systems are single reaction systems $(A + B \rightarrow R)$, consecutive reaction systems $(A + B \rightarrow R)$ R, $B + R \rightarrow S$) and parallel competing reaction systems (A + B \rightarrow R, A + $C \rightarrow S$). Due to the rigorous conditions imposed for the on-line analysis of the single reaction, the last two schemes are favoured and usually employed when measuring the final product quality. Bourne and his co-workers proposed several reaction systems based on the consecutive competing scheme, such as the bromination of 1,3,5-trimethoxybenzene (Bourne and Kozicki, 1977), the azo-coupling of 1-naphthol with diazotised sulphanilic acid (Bourne et al., 1981) and the selective iodination of l-tyrosine (Bourne and Rohani, 1983). However, these proposed systems and the experimental methods still have some disadvantages, especially with their toxic, volatile and unstable nature. With a better understanding of the mixing and chemical reactions, Villermaux et al. (1994) and Fournier et al. (1996) proposed the use of a parallel competing scheme based on the iodide-iodate reaction system. Generally, the products produced in such a system are easily analysed by using the spectrophotometric method. This method have been successfully applied for the assessment of the micromixing efficiency in stirred vessel reactors (Unadkat et al., 2013; and Lemenand et al., 2017) and in high shear mixer (Qin et al., 2017). As the use of

the parallel competing reaction system has the advantages of simple control, sensitive measurement through detection of the product concentration and low toxicity of agents, the Villermaux iodide-iodate reaction system is adopted in the present study.

4.2.1 Reaction kinetics

The reaction system can be described by three sub-reactions, which are expressed as

$$H_2BO_3^- + H^+ \stackrel{k_1}{\Leftrightarrow} H_3BO_3 \text{ (quasi - instantaneous)}$$
(4.1)

$$5I^{-} + IO_{3}^{-} + 6H^{+} \stackrel{k_{2}}{\leftrightarrow} 3I_{2} + 3H_{2}O \text{ (fast)}$$
 (4.2)

$$I_2 + I^{-\frac{\kappa_3}{\leftarrow}} I_3^{-} \tag{4.3}$$

where H⁺ stands for the hydrogen ion of the sulfuric acid (H₂SO₄). Such a system can be regarded as having a competition between the first neutralisation reaction and the second Dushman reaction that produces the by-product of iodine, leading to the occurrence of the third reaction. The concentration of triiodide (I₃⁻) in the third reaction can be measured by a UV spectrophotometer. Reaction (1) is quasi-instantaneous with a second-order rate constant k_1 at about 10^{11} Lmol⁻¹s⁻¹ (Unadkat *et al.*, 2013), while Reaction (2) is very fast and has the same order of magnitude as the micromixing process as indicated by Fournier *et al.* (1996). The rate constant k_2 depends on the ionic strength *I* (Guichardon

et al., 2000) and will change during the micromixing process, which was found to be well approximated by the following empirical relationships:

$$logk_2 = 9.28 - 3.66\sqrt{I_i}, \ I_i < 0.16 \ mol \cdot L^{-1}$$
(4.4)

$$logk_2 = 8.38 - 1.51\sqrt{I_i} + 0.23I_i, \ I_i > 0.16 \ mol \cdot L^{-1}$$
(4.5)

The rate laws of Reactions (4.1) and (4.2) can be expressed as

$$r_1 = k_1 c_{H_2 B O_3^-} c_{H^+} \tag{4.6}$$

$$r_{1} = k_{1}c_{H_{2}BO_{3}^{-}}c_{H^{+}}$$

$$r_{2} = k_{2}c_{I^{-}}^{2}c_{IO_{3}^{-}}c_{H^{+}}^{2}$$

$$(4.6)$$

$$(4.7)$$

The equilibrium constant K_3 of Reaction (4.3) is given by

$$K_3 = \frac{k_3}{k_3'} = \frac{c_{I_3^-}}{c_{I_2}c_{I^-}}$$
(4.8)

For a given reaction, the value of K_3 is only dependent on temperature. For $I_3^$ formation, K_3 is given by Palmer *et al.* (1984) and is expressed as follows:

$$logK_3 = \frac{555}{T} + 7.355 - 2.575 logT \tag{4.9}$$

Due to these three reactions occurring in one system, there is a material balance on each component. On the basis of yield of iodide ion (i.e., I⁻), its material

balance can be written as

$$c_{I^{-}} = \frac{c_{I_{0}^{-}}V_{1}}{V_{0}+V_{1}} - \frac{5}{3}(c_{I_{3}^{-}} + c_{I_{2}}) - c_{I_{3}^{-}}$$
(4.10)

where $c_{I_0^-}$ stands for the initial concentration of I⁻. V_0 represents the volume of H₂SO₄ solution, while V_I is the volume of the mixture solution of reactants. H₂SO₄, serving as the limiting agent, is additionally injected to the system to trigger the parallel competing reaction between Reactions (4.1) and (4.2).

Combining Equations (4.8) and (4.9) with (4.10), the concentration of iodine (I_2) can be calculated from Equation (4.11).

$$-\frac{5}{3}c_{I_2}^2 + \left(\frac{c_{I_0}V_1}{V_0 + V_1} - \frac{8}{3}c_{I_3}\right)c_{I_2} - \frac{c_{I_3}}{K_3} = 0$$
(4.11)

The main by-product of the Villermaux iodide-iodate reaction system is I_2 . With the presence of excessive I^- , I_2 will further react with I^- to generate I_3^- until an equilibrium is reached. Since I_3^- has absorption peaks at the wavelength of 288 nm and 353 nm in the spectrum, the concentration of I_3^- can be measured by a UV spectrophotometer. However, I^- also presents the absorption peak at around 288 nm in the spectrum. In order to reduce interference from the other components, the use of 353 nm as an indicator is preferable for the concentration measurement of I_3^- . According to Beer-Lambert's law, the absorption *A* of a component across a quartz cell with a thickness Ψ is linearly dependent on its concentration c and molar extinction coefficient e, i.e.

$$A_{353} = e_{353}c_{I_3^-}\Psi \tag{4.12}$$

For a particular product and a quartz cell, the molar extinction coefficient e and thickness Ψ are fixed values. Thus, the absorption is linearly dependents on the concentration of I_3^- . The calibration curve of I_3^- was firstly prepared before experimental work was performed as shown in Figure 4.1. The calibration curve with R^2 equal to 0.987 highlights that the Beer- Lambert's law is valid within the range of I_3^- concentration chosen in the present study. For the micromixing experiment test, once the absorption of triiodide ion is obtained from the UV spectrophotometer, the concentration of I_3^- can be calculated from the calibration curve.



Figure 4.1 Calibration curve of the triiodide ion concentration at 353 nm in the

UV spectrum.

4.2.2 Definition of segregation index

The segregation index (*Xs*) is defined as the relative amount of H⁺ consumed by Reaction (4.2). For a perfect micromixing condition, all H⁺ would need to be evenly distributed in the system and then immediately consumed by borate ion (i.e., $H_2BO_3^-$) without the appearance of Reaction (4.2). On the contrary, for poor micromixing, $H_2BO_3^-$ and I⁻, iodate ion (i.e., IO_3^-) would compete with H⁺ simultaneously. According to stoichiometry, the yield of I₂ from Reaction (4.2) for a total segregation is expressed as,

$$Y_{ST} = \frac{6n_{IO_{3,0}}}{6n_{IO_{3,0}} + n_{H_2BO_{3,0}}}$$
(4.13)

In practice, I_2 exists in two parts. One is generated in Reaction (4.2), and the other one is consumed by Reaction (4.3). Thus, the yield of I_2 should be calculated through the ratio of total mole of both I_2 and IO_3^- to the initial mole of H⁺, as defined by

$$Y = \frac{2(n_{I_2} + n_{I_3})}{n_{H_0^+}} \tag{4.14}$$

Therefore, Xs can be written as

$$X_{S} = \frac{Y}{Y_{ST}} = \frac{n_{I_{2}} + n_{I_{3}}}{n_{H_{0}^{+}}} \left(2 + \frac{n_{H_{2}BO_{3,0}}}{3n_{IO_{3,0}}}\right)$$
(4.15)

Equation (4.15) can be converted in terms of the concentration given by Equation (4.16).

$$X_{S} = \frac{(c_{I_{2}} + c_{I_{3}})(V_{0} + V_{1})}{n_{H_{0}^{+}}} \left(2 + \frac{c_{H_{2}BO_{3,0}^{-}}}{3c_{IO_{3,0}^{-}}}\right)$$
(4.16)

By definition, the value of X_S varies between 0 and 1 with a lower value indicating a better micromixing performance.

$X_s = 0$	Perfect micromixing		
$X_s = 1$	Total segregation		
$0 < X_s < 1$	Partial segregation		

4.2.3 CFD modelling

In order to get a better understanding of the mixing conditions in the TC reactor, the flow fields of two different inner cylinders were simulated using commercial CFD code, FLUENT 17.0. Based on the structures of the two types of inner cylinder shown in Figure 4.2, the geometry was created by ANSYS ICEM. Then, the computational domain was divided into two zones, connected by the predefined interface. The total meshes have around 1,100,000 cells, with each direction of $16 \times 147 \times 480$ (radial×circumferential×axial). Our previous work

(Liu *et al.*, 2020) presents the details for such flow field simulation, where RNG k- ε turbulent model was adopted. The boundary conditions were set as velocity inlet and pressure outlet with no slip wall. The discretized equations were realized by the SIMPLEC algorithm.

4.3 Experimental

4.3.1 Apparatus setup

The apparatus of the TC reactor is illustrated in Figure 4.2 (a). Two types of inner cylinder are adopted in this study, one being the classical inner cylinder with a circular cross-sectional profile and the other is a lobed cross-sectional profile inner cylinder, whose cross section consists of three identical arcs connected by three tangential lines. Figure 4.2 (b) displays the cross-sectional profiles for both geometries. Here, the abbreviations of CTC and LTC denote the classical TC reactor and the lobed TC reactor, respectively. The dimensions of the TC reactor are described in Table 4.1.



Figure 4.2 (a) Schematic diagram of experimental setup; and (b) Schematic of cross-section profiles for the: (i) CTC; and (ii) LTC.

 Table 4.1 Dimensions of the TC reactor.

Dimension	СТС	LTC
Reactor length, L (mm)	300.00	300.00
Outer cylinder radius, r_o (mm)	50.00	50.00
Inner cylinder radius (original or equivalent), r_i (mm)	40.00	40.19
Gap size, <i>d</i> (mm)	10.00	9.81

In order to determine the flow pattern in the TC reactor, the Reynolds number based on the gap size has been adopted, as defined by

$$Re = \frac{\omega_i r_i d}{\nu} \tag{4.17}$$

where ω_i and r_i are the angular velocity and the radius of the inner cylinder, respectively. *d* is the gap size, and *v* is the kinematic viscosity of the suspension. In this study, various cases with different Reynolds number have been investigated by changing the rotational speed of the inner cylinder. The critical Reynolds number (*Re_c*), which indicates the presence of Taylor vortex flow was found to be about 97 with the classical inner circular cylinder (i.e., radius ratio $\eta = \frac{r_i}{r_o} = 0.8$). When the Reynolds number exceeds the critical Reynolds number, the flow pattern will experience a series of instabilities, including wavy Taylor vortex flow and turbulent Taylor vortex flow, which can finally develop into turbulent Taylor flow (Grossmann *et al.*, 2016).

4.3.2 Villermaux reaction procedures

All the agents were purchased from Sinopharm Chemical Reagent Co., Ltd of China with a purity level of above 99.0%. Firstly, boric acid (H₃BO₃, 0.089 mol/L), potassium iodide (KI, 0.0116 mol/L), and potassium iodate (KIO₃, 0.00233 mol/L) solutions were prepared separately with their respective molar concentrations. Then, KI and KIO₃ were mixed together with sodium hydroxide (NaOH) solution. NaOH was used to adjust the pH value around 10.0 in order to prevent the reaction between KI and KIO₃ with the presence of H⁺. It should be noted here the pH value should be carefully controlled during solution preparation. At such alkaline environment, H₃BO₃ further mixed with the above solution to form Solution A, while Solution B composed of H₂SO₄ solution with different concentrations. Before inducing Villermaux reaction, Solution A was firstly pumped into the TC reactor, fully filling up the gap area. Then, H₂SO₄ solution was injected into the reactor by thin needle to trigger chemical reaction.

The rotational speed was adjusted within the range of 50 rpm to 1000 rpm, corresponding to the Reynolds Number varying from 2000 to 42000. After the system reached a steady state, H₂SO₄ solution was injected into the reactor from the bottom inlet. In each run, about 3.0 mL of sample solution was collected for the UV test from the top outlet after completing the mixing. The absorption intensity test was conducted immediately using the UV spectrophotometer (UNICO SQ4802 UV/VIS Spectrophotometer, U.S.A) at the wavelength of 353 nm to ensure the stability of I_3^- . The experiment and the sample measurement were carried out at the room temperature of 25°C. The operating conditions are summarised in Table 4.2.

 Table 4.2 Operating conditions.

Experimental	Feeding	H ⁺ concentration	Rotational	Reynolds
number	time (s)	(mol/L)	speed (rpm)	number
R1	120	2.0	50	2094
R2	120	2.0	100	4188

R3	120	2.0	200	8376
R4	120	2.0	300	12564
R5	120	2.0	400	16752
R6	120	2.0	600	25128
R7	120	2.0	800	33504
R8	120	2.0	1000	41880
R9	20	2.0	300	12564
R10	40	2.0	300	12564
R11	60	2.0	300	12564
R12	240	2.0	300	12564
R13	360	2.0	300	12564
R14	480	2.0	300	12564
R15	120	1.2	300	12564
R16	120	1.6	300	12564
R17	120	4.0	300	12564
R18	120	5.0	300	12564
R19	120	6.0	300	12564

4.4 Results and discussion

In the segregation experiments, the sampling location was set with a distance away from the inlet of acid injection. In order to guarantee that a wellestablished micromixing process is achieved throughout the whole reactor, the collection time after acid injection should be determined in advance. The preliminary experiment was performed at a Reynolds number of 12564 in the CTC. It can be seen from Figure 4.3 that the critical collection time is 120 s after finishing the injection of acid. However, within the range from 90 s to 240 s, the results used to determine the collection time also appear to be acceptable. One can argue that if the collection time is too short, the macromixing has not been fully achieved, thus resulting in little amount of the product being detected at the outlet. On the other hand, if the collection time is too long, the UV result may lose its accuracy since I_3^- is very sensitive to light. Therefore, the determination of the critical collection time is crucial for acquiring reliable results. It should be noted that for different operating conditions, the critical collection time may be different within the acceptable range. The following discussion on the micromixing in the TC reactor will be based on the samples collected at the critical collection time determined.



Figure 4.3 Preliminary test of the selection of sample collection time.

4.4.1 Effect of feeding time on Xs

Mixing in the TC reactor involves all the scales from macro-scale, meso-scale to micro-scale. In order to better separate the influence of macromixing on micromixing and only observe the micromixing behaviour, the feeding rate of acid solution should be controlled as low as possible as mentioned earlier. In our experiment, the injection of acid solution was maintained at a constant feeding rate, which means the feeding time should be controlled long enough.

Figure 4.4 shows the change of *Xs* with feeding time in the CTC and LTC, where *Xs* gradually decreases and reaches an almost constant value with little fluctuation. When taking a very fast injection, the value of *Xs* will be jointly controlled by both macro- and micro-mixing. Under such a condition, the local concentration gradient can be very high, as the acid plume cannot be dispersed well throughout the whole reactor scale (Baldyga & Bourne, 1999). Accordingly, this will lead to the local excess of H⁺ and a large value of *Xs*. However, this is mainly caused by poor dispersion rather than poor micromixing in the reactor, as the effect of macromixing is not eliminated. On the other hand, a fast injection leading to a random fluctuation will break the steady state of flow field. When more turbulent eddies are involved, the dynamic balance of acid engulfment with bulk reactants cannot be achieved. As local $H_2BO_3^-$ is not enough to consume a large amount of H⁺, the excessive H⁺ will react with I⁻ and IO_3^- ,

yielding a large value of *Xs*. With a slow injection of acid, the turbulence is less affected such that the acid has enough time to be dispersed evenly in a macro-scale throughout the reactor and a well-established environment for micromixing is obtained. Consequently, the UV measurement result given by chemical test reactions is free from the macromixing influence and is only dependent on the micromixing behaviour. Thus, the feeding time of 120 s was chosen for all the subsequent experiments.



Figure 4.4 Effect of feeding time on segregation index.

4.4.2 Effect of H⁺ concentration on Xs

Because the linear relationship between I_3^- concentration and its absorption is valid within a particular range, the H⁺ concentration should be selected

appropriately to avoid excessive or too little I₂ being generated. A wide range of H^+ concentration from 1.2 mol/L to 6.0 mol/L has been tested. The experiment was conducted under the condition of the Reynolds number of 12564 with 1.0 mL injection. It can be seen from Figure 4.5 that the value of Xs firstly increases, then levels off with the increase of H^+ concentration. At a higher H^+ concentration, more time is needed for $H_2BO_3^-$ to neutralize H^+ . However, the amount of $H_2BO_3^-$ was kept at a constant level when changing the H⁺ concentration. Thus, the excessive H⁺ will lead to the occurrence of Reaction (4.2). It can be seen from the rate laws of Equations (4.6) and (4.7)that Reaction (4.2) is more sensitive to H⁺ due to its higher rate order. Moreover, the chemical reaction rate of Reaction (4.2) is usually higher when compared to the micromixing rate (Fournier et al., 1996), which will be presented and discussed in Section 4.4.4. Thus, excessive H⁺ leads to the generation of a large amount of I_2 , and a high value of Xs. It is worth mentioning that the continuous increase of H⁺ concentration does not give rise to the continuous increase of Xs. Due to the local excess of H^+ concentration, both Reactions (4.1) and (4.2) have been completed, which means that all reactants have achieved their maximum conversion. As a result, I₂ concentration will not increase any further, the most sensitive point for the UV detection corresponds to the H⁺ concentration of 2.0 mol/L as indicated in Figure 4.5. This value has been chosen for all the subsequent experiments.



Figure 4.5 Effect of H⁺ concentration on segregation index.

One can see from Figure 4.5 that micromixing performance in the LTC is better than that of the CTC at all ranges of the H^+ concentration, but such a difference is less noticeable at high H^+ concentration. For the LTC, the rotational lobed inner cylinder generates a periodic variation of the gap size. The circumferential flow will experience an expansion and contraction, leading to the generation of the induced turbulent eddies from the surface of the concaved top of the inner cylinder and the enhanced turbulent eddy interactions. Such turbulent eddy interaction can effectively re-disperse the concentration field of reactants, promoting a better distribution of the reactants, less local H^+ accumulation and less local formation of I₂. This is another piece of evidence to suggest that lobed geometry can effectively reduce the overall mixing time and improve the
micromixing efficiency for the TC reactor.

4.4.3 Effect of Reynolds number on Xs

Figure 4.6 (a) shows the effect of the variation of Reynolds number on Xs under the condition of 1.0 mL sulfuric acid solution injected within 120 s. With the increase of Reynolds number, Xs decreases in both the CTC and LTC. When Reynolds number is greater than 25128 (corresponding to 600 rpm), the decrease in Xs becomes small. At a low rotational speed, i.e., a small Reynolds number, Xs presents a very high value, and the difference between the CTC and LTC is very small, which can be attributed to the excessive turbulence generated by the lobed inner cylinder being still small. Although the geometry modification can enhance the micromixing to some extent, flow pattern has not become fully turbulent for both the CTC and LTC. The degree of the occurrence of the micromixing may still rely on the molecule-scaled diffusion. The reactant fluid elements that contribute to the micromixing still hold a relatively large size compared with the molecular diffusion length scale. In such case, the micromixing may not be sufficient. With the increase of Reynolds number, turbulence intensity is gradually built up and the flow in the reactor develops to the turbulent state, and the micromixing improves evidenced by drop in Xs. Although the chemical reaction occurs at molecular level, the intensified turbulence can provide the environment for reactant fluid elements to break into much smaller size eddies with the surface area for the mass transfer being increased. As a result, mixing diffusion improves and the micromixing rate can be accelerated. Finally, as Reynolds number exceeds 25128, it is observed that *Xs* levels off, reaching a minimum of about 0.15 and 0.08 for the CTC and LTC, respectively.



Figure 4.6 (a) Effect of Reynolds number on segregation index; and (b) Segregation index as a function of Reynolds number.

It is cautiously mentioned here that the difference of *Xs* between the CTC and LTC becomes remarkable with the flow in the TC reactor to be judged to be fully turbulent. The LTC shows a much better micromixing than the CTC. This may be explained by the facts: Firstly, with the rotation of the inner cylinder, gap size of the LTC varies periodically so that the formed Taylor vortices change and the vortices are deformed. Consequently, this type of perturbation due to the deformation Taylor vortices will induce the generation of small turbulent eddies down to the scales beneficial to the micromixing. Secondly, Liu *et al.*

(2020) have compared the turbulent flows generated by the CTL and LTC and shown that the impinging jet region existing between the two toroidal counterrotating Taylor vortices induces a stronger outward shear gradient in the LTC than that in CTL when the same rotational speed was taken. Thus, it can be claimed that the reactant micro elements entrapped by the turbulent eddies generated by the impinging jet flow shear in the LTC can have a shorter entrainment time than the CTC.

In order to quantitatively describe how *Xs* changes with the Reynolds number, the following relation is proposed, given by

$$Xs = CRe^b \tag{4.18}$$

By taking the logarithmic transformation of both sides, a liner relationship is obtained. Using this regression fitting, it is found that well fitted relation for the CTC is lnXs = -0.451lnRe + 2.963 with $R^2=0.968$ and the same fitted relation for the LTC is lnXs = -0.635lnRe + 4.319 with $R^2=0.986$, respectively. As the slops *b* for both relations show negative values, the smaller value of *b* indicates *Xs* to be more sensitive to turbulent eddies.

As the turbulent intensity can be used to determine the micromixing efficiency as suggested by Qin *et al.* (2017), the turbulent intensity measured on the surface of the inner cylinder for both the CTC and LTC based on CFD simulation is shown in Figure 4.7. For three representative rotational speeds, 100, 600 and 1000 rpm, the corresponding Reynolds numbers are 4188, 25128 and 41880, respectively. It can be seen clearly from the figure that the turbulent intensity is enhanced with the increase of Reynolds number for both the CTC and LTC but the enhancement for the LTC is significantly larger than that in the CTC. Also, the highest turbulent intensity appears at regions of three concaved arcs, corresponding to the smallest gap regions in the LTC. We postulate that the best micromixing may happen in these regions. To demonstrate this, the correlation between the turbulence intensity and 1/Xs is proposed.

$$R_{IXs} = < I > \frac{1}{x_s} \tag{4.19}$$

where $\langle I \rangle$ is the volume average turbulence intensity. Figure 4.8 shows such correlation, clearly indicating that the micromixing can be improved through the modification of the inner cylinder configuration of the TC reactor.



Figure 4.7 Distribution of the turbulent intensity on the surface of the inner cylinder: (a) CTC; and (b) LTC at different Reynolds numbers: (i): 4188; (ii) 25128; and (iii) 41880.



Figure 4.8 Correlation between the turbulence intensity and segregation index at different Reynolds numbers.

4.4.4 Characterisation of micromixing time

In order to compare the micromixing efficiency of the adopted TC reactor especially the lobed inner cylinder with conventional stirred tank, the micromixing times for different reactors are evaluated. Many models have been proposed to estimate micromixing time. Among these models, the IEM model (Costa and Trevissoi, 1972), the EDD model (Baldyga and Bourne, 1984), the E-model (Baldyga and Bourne, 1989), and the incorporation model (Villermaux *et al.*, 1994) are representatives. However, the incorporation model has been widely used and recognized as illustrated in Figure 4.9. This model assumes that the limited agent, acid occupying Environment 2, is divided into several aggregates, which then are progressively invaded by surrounding solution from Environment 1. Consequently, the volume of acid aggregates gradually grows due to the incorporation, based on $V_2 = V_{20}g(t)$. The characteristic incorporation time is assumed to be equivalent to the micromixing time. Fournier *et al.* (1990) proposed a dilution-reaction equation in the reaction Environment 2, which is found to be suitable for the description of the present employed TC reactor system, given by

$$\frac{dc_j}{dt} = (c_{j10} - c_j) \frac{1}{g} \frac{dg}{dt} + r_j$$
(4.20)

where c_j is the reactant concentration, and species *j* denotes H₂BO₃⁻, H⁺, I⁻, IO₃⁻, I₂, and I₃⁻. c_{j10} is the concentration of surrounding solution (i.e., the initial concentration of species *j* in Environment 1). r_j is the net production rate of species *j*, and *g* denotes the mass exchange rate between reactant fluid particle and its surrounding solution. A large value of dg/dt indicates a fast dilution, thus a good mixing performance between the feeding acid and its surrounding solution. The empirical equation of the growing law for acid aggregates can be expressed as an exponential function of micromixing time, t_m , which reads

$$g(t) = exp(\frac{t}{t_m}) \tag{4.21}$$

Thus, Equation (4.20) can be converted into the following form,

$$\frac{dc_j}{dt} = \frac{c_{j10} - c_j}{t_m} + r_j \tag{4.22}$$

From Equation (4.22), the mass balance equation of individual species can be obtained. In total, there are six transport equations to be solved. In order to reduce computational cost, the W-Z transformation was adopted to reduce the number of solutions and the simplification yields

$$\frac{dW}{dt} = -\frac{c_{H_2BO_3,10} + W}{t_m} - 6r_2 \tag{4.23}$$

$$\frac{dY}{dt} = \frac{c_{I^-,10} - Y}{t_m} - 8r_2 \tag{4.24}$$

$$\frac{dZ}{dt} = \frac{c_{I^-,10} - Z}{t_m} - 5r_2 \tag{4.25}$$

$$\frac{dc_{IO_3^-}}{dt} = \frac{c_{IO_3^-,10} - c_{IO_3^-}}{t_m} - r_2 \tag{4.26}$$

where $W = c_{H^+} - c_{H_2BO_3^-}$, $Y = c_{I^-} - c_{I_2}$, and $Z = c_{I^-} + c_{I_3^-}$. Equations (4.23)-(4.26) can be solved numerically by iteration, where the initial conditions are given by $W = c_{H^+,0}$, Y = 0, Z = 0, and $c_{IO_3^-} = 0$. The iteration ends as H⁺ concentration approaches 0. Acid concentration reaches its highest value at the inlet, then, it disperses within a very limited range and is consumed quickly. Thus, H⁺ concentration is assumed to be at its initial value, $c_{H^+,0}$ during the iteration before it is completely consumed. The forth-order Runge-Kutta

method was adopted in the present study to calculate t_m . Firstly, a series value of t_m is assumed. Following the Runge-Kutta iteration, Equations (4.23)-(4.26) are solved, and the concentrations of individual species are obtained. Subsequently, a set of segregation index Xs can be calculated based on Equation (4.16). Figure 4.10 depicts the obtained relation of Xs against the micromixing time t_m ($Xs = 37991 t_m$). This relation can be used to evaluate the micromixing time in TC reactor based on the value of Xs obtained from the experimental results, which are marked in Figure 4.10. Figure 4.11 shows the relationship between the Reynolds number and micromixing time in the CTC and LTC. For better description, the contour of turbulent intensities in the circumferential direction for both the CTC and LTC is also shown in Figure 4.11, where the intensified regions by geometry modification can be seen clearly. By using power law fitting, the micromixing time for both the CTC and LTC can be by $t_m = 0.0025 Re^{-0.664}$ approximated and $t_m = 0.0006 Re^{-0.456}$ respectively.



Figure 4.9 Principle of micromixing process based on the incorporation model.



Figure 4.10 Predicted segregation index and micromixing time based on the incorporation model.



Figure 4.11 Micromixing time as a function of Reynolds number.

Damköhler number (Da), defined as the ratio of the chemical reaction timescale (reaction rate) to the mixing timescale (mixing rate), is also used to characterize the impact of hydrodynamics in the TC reactor on chemical reaction. Here, we use the obtained relations for the micromixing time to estimate Da_1 and Da_2 for Reactions (4.1) and (4.2), respectively. The chemical reaction time for Reactions (4.1) and (4.2) is given by

$$t_{r_1} = \frac{\min(c_{H_2BO_3^-,0}; c_{H^+,0})}{r_1} \tag{4.27}$$

$$t_{r_1} = \frac{\min(\frac{3}{5}c_{I^-,0}; 3c_{IO_3^-,0}; \frac{1}{2}c_{H^+,0})}{r_2}$$
(4.28)

Thus, Da_1 and Da_2 can be estimated using Equations (4.29) and (4.30).

$$Da_1 = \frac{t_m}{t_{r_1}} = t_m k_1 c_{H^+,0} \tag{4.29}$$

$$Da_2 = \frac{t_m}{t_{r_2}} = t_m k_2 c_{I^-,0}^2 c_{H^+,0}^2$$
(4.30)

The estimated $Da_1=4.2\times10^5-2.8\times10^6$ is much great than 1, indicating that Reaction (4.1) is an instantaneous reaction. $Da_2=3.2\times10^{-3}-2\times10^{-2}$ has the order of 10^{-2} , which is small than 1. Both results indicate that the iodide-iodate reaction system used for evaluation of the micromixing performance in the TC reactor to be suitable.

Compared with the conventional stirred tank reactor, in which the micromixing

time is the order of 20 ms (Fournier *et al.*, 1996), the order of micromixing time in the TC reactor is evaluated to be 10^{-5} s based on the above discussion. It thus can be claimed that the TC reactor can have a better micromixing performance than the traditional stirred tank reactor as far as those fast chemical processes controlled by the mixing are concerned. The use of the lobed inner cylinder configuration in the TC reactor can further shorten the micromixing time due to the local turbulence intensification.

4.5 Conclusions

The micromixing performance in a TC reactor with two different inner cylinder geometries has been evaluated based on the parallel competing iodide-iodate reaction system to characterise the impact of the inner cylinder configuration variations which will significantly affect the micromixing process by changing hydrodynamic environment. Segregation index *Xs* was employed as an indicator to characterise the micromixing efficiency. In order to assess the effects of various factors, the sample collection time has been carefully determined to ensure the reliable UV results. The acid concentration was also carefully chosen to avoid over-loading, while the injection of acid was controlled to keep the feeding as slow as possible in order to eliminate the impact of macromixing in the TC reactor. The conclusions reached for the present study can be summarised as follows:

(1) The segregation experimental results have indicated that the value of *Xs* decreases with the increase of Reynolds number for both inner cylinder configurations but the LTC exhibits a better micromixing performance than the CTC as *Xs* for the LTC is smaller than the CTC.

(2) CFD simulation results have revealed that the turbulence intensity generated in the jet regions in vicinity of the inner cylinder in the LTC is stronger than that in the CTC, which subsequently enhances the local micromixing, This clearly indicates that the modification of the inner cylinder configuration (here, the use of a lobed cross-sectional profile) may improve the micromixing action significantly.

(3) Predictions made by employing the incorporation model show that the micromixing time is estimated to be of the order of 10^{-5} s for the TC reactor, much smaller than that of the traditional stirred tank reactor according to the open literature. In addition, the LTC shows a shorter micromixing time than the CTC.

References

- Aljishi, M.F., Ruo, A.C., Park, J.H., Nasser, B., Kim, W.S. and Joo, Y.L., 2013. Effect of flow structure at the onset of instability on barium sulfate precipitation in Taylor–Couette crystallizers. *Journal of Crystal Growth*, 373, pp.20-31.
- Baldyga, J. and Bourne, J.R., 1984. A fluid mechanical approach to turbulent mixing and chemical reaction part II micromixing in the light of turbulence theory. *Chemical Engineering Communications*, 28(4-6), pp.243-258.
- Baldyga, J. and Bourne, J.R., 1989. Simplification of micromixing calculations.I. Derivation and application of new model. *The Chemical Engineering Journal*, 42(2), pp.83-92.
- Bałdyga, J. and Bourne, J.R., 1999. *Turbulent mixing and chemical reactions*. Wiley.
- Bertrand, M., Lamarque, N., Lebaigue, O., Plasari, E. and Ducros, F., 2016. Micromixing characterisation in rapid mixing devices by chemical methods and LES modelling. *Chemical Engineering Journal*, 283, pp.462-475.
- Bourne, J.R., 1977. Mixing effects during the bromination of 1,3,5trimethoxybenzene. *Chemical Engineering Science*, *32*(12), pp. 1538-1539.
- Bourne, J.R., Kozicki, F. and Rys, P., 1981. Mixing and fast chemical reaction—
 I: Test reactions to determine segregation. *Chemical Engineering Science*, *36*(10), pp.1643-1648.

Bourne, J.R. and Rohani, S., 1983. Micro-mixing and the selective iodination

of 1-tyrosine. *Chemical Engineering Research and Design*, *61*(5), pp.297-302.

- Costa, P. and Trevissoi, C., 1972. Reactions with non-linear kinetics in partially segregated fluids. *Chemical Engineering Science*, *27*(11), pp.2041-2054.
- DiPrima, R.C., Eagles, P.M. and Ng, B.S., 1984. The effect of radius ratio on the stability of Couette flow and Taylor vortex flow. *The Physics of fluids*, 27(10), pp.2403-2411.
- Drozdov, S.M., 2002. A numerical investigation of a modified Couette-Taylor apparatus with application to industrial mixing. *Theoretical and Computational Fluid Dynamics*, *16*(1), pp.17-28.
- Fournier, M.C., Falk, L. and Villermaux, J., 1996. A new parallel competing reaction system for assessing micromixing efficiency—experimental approach. *Chemical Engineering Science*, *51*(22), pp.5053-5064.
- Fournier, M.C., Falk, L. and Villermaux, J., 1996. A new parallel competing reaction system for assessing micromixing efficiency—determination of micromixing time by a simple mixing model. *Chemical Engineering Science*, *51*(23), pp.5187-5192.
- Gao, Z., Han, J., Bao, Y. and Li, Z., 2015. Micromixing efficiency in a T-shaped confined impinging jet reactor. *Chinese Journal of Chemical Engineering*, 23(2), pp.350-355.
- Grossmann, S., Lohse, D. and Sun, C., 2016. High–reynolds number taylorcouette turbulence. *Annual Review of Fluid Mechanics*, 48, pp.53-80.

Guichardon, P. and Falk, L., 2000. Characterisation of micromixing efficiency

by the iodide–iodate reaction system. Part I: experimental procedure. *Chemical Engineering Science*, *55*(19), pp.4233-4243.

- Haut, B., Amor, H.B., Coulon, L., Jacquet, A. and Halloin, V., 2003.
 Hydrodynamics and mass transfer in a Couette–Taylor bioreactor for the culture of animal cells. *Chemical Engineering Science*, 58(3-6), pp.777-784.
- Jacobsen, N.C. and Hinrichsen, O., 2012. Micromixing efficiency of a spinning disk reactor. *Industrial & Engineering Chemistry Research*, 51(36), pp.11643-11652.
- Jung, W.M., Kang, S.H., Kim, W.S. and Choi, C.K., 2000. Particle morphology of calcium carbonate precipitated by gas–liquid reaction in a Couette– Taylor reactor. *Chemical Engineering Science*, *55*(4), pp.733-747.
- Kim, J.E. and Kim, W.S., 2017. Synthesis of Core–Shell Particles of Nickel– Manganese–Cobalt Hydroxides in a Continuous Couette-Taylor Crystallizer. *Crystal Growth & Design*, 17(7), pp.3677-3686.
- Lemenand, T., Della Valle, D., Habchi, C. and Peerhossaini, H., 2017. Micromixing measurement by chemical probe in homogeneous and isotropic turbulence. *Chemical Engineering Journal*, *314*, pp.453-465.
- Li, G., Yang, X. and Ye, H., 2015. CFD simulation of shear flow and mixing in a Taylor–Couette reactor with variable cross-section inner cylinders. *Powder Technology*, 280, pp.53-66.
- Liu, Z., Guo, L., Huang, T., Wen, L. and Chen, J., 2014. Experimental and CFD studies on the intensified micromixing performance of micro-impinging

stream reactors built from commercial T-junctions. *Chemical Engineering Science*, *119*, pp.124-133.

- Liu, L., Yang, X., Li, G., Huang, X. and Xue, C., 2020. Shear controllable synthesis of barium sulfate particles using lobed inner cylinder Taylor-Couette flow reactor. *Advanced Powder Technology*, 31(3), pp.1088-1099.
- Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-Rich hydroxide in reaction crystallization: Effect of Taylor vortex dimension and intensity. *Crystal Growth & Design*, *15*(4), pp.1726-1734.
- Nguyen, A.T., Kim, J.M., Chang, S.M. and Kim, W.S., 2011. Phase Transformation of Guanosine 5-Monophosphate in Continuous Couette– Taylor Crystallizer: Experiments and Numerical Modeling for Kinetics. *Industrial & Engineering Chemistry Research*, 50(6), pp.3483-3493.
- Palmer, D.A., Ramette, R.W. and Mesmer, R.E., 1984. Triiodide ion formation equilibrium and activity coefficients in aqueous solution. *Journal of Solution Chemistry*, *13*(9), pp.673-683.
- Park, S. and Kim, W.S., 2018. Influence of fluid motions on polymorphic crystallization of L-histidine: Taylor vortex flow and turbulent Eddy flow. *Crystal Growth & Design*, 18(2), pp.710-722.
- Racina, A. and Kind, M., 2006. Specific power input and local micromixing times in turbulent Taylor–Couette flow. *Experiments in Fluids*, 41(3), pp.513-522.
- Richter, O., Hoffmann, H. and Kraushaar-Czarnetzki, B., 2008. Effect of the

rotor shape on the mixing characteristics of a continuous flow Taylorvortex reactor. *Chemical Engineering Science*, *63*(13), pp.3504-3513.

- Richter, O., Menges, M. and Kraushaar-Czarnetzki, B., 2009. Investigation of mixing in a rotor shape modified Taylor-vortex reactor by the means of a chemical test reaction. *Chemical Engineering Science*, 64(10), pp.2384-2391.
- Qin, H., Zhang, C., Xu, Q., Dang, X., Li, W., Lei, K., Zhou, L. and Zhang, J., 2017. Geometrical improvement of inline high shear mixers to intensify micromixing performance. *Chemical Engineering Journal*, 319, pp.307-320.
- Shi, X., Xiang, Y., Wen, L.X. and Chen, J.F., 2012. CFD analysis of flow patterns and micromixing efficiency in a Y-type microchannel reactor. *Industrial & Engineering Chemistry Research*, 51(43), pp.13944-13952.
- Soos, M., Wu, H. and Morbidelli, M., 2007. Taylor- Couette unit with a lobed inner cylinder cross section. *AIChE Journal*, *53*(5), pp.1109-1120.
- Tang, Z., Kim, W.S. and Yu, T., 2019. Studies on morphology changes of copper sulfide nanoparticles in a continuous Couette-Taylor reactor. *Chemical Engineering Journal*, 359, pp.1436-1441.
- Thai, D.K., Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of ni-rich hydroxide crystals in taylor vortex flow. *Powder Technology*, 274, pp.5-13.
- Unadkat, H., Nagy, Z.K. and Rielly, C.D., 2013. Investigation of turbulence modulation in solid–liquid suspensions using parallel competing reactions

as probes for micro-mixing efficiency. *Chemical Engineering Research and Design*, *91*(11), pp.2179-2189.

- Villermaux, J., Falk, L. and Fournier, M.C., 1994. Potential use of a new parallel reaction system to characterize micromixing in stirred reactors. In *AIChE Symposium Series 90*(299), pp. 50-54.
- Villermaux, J. and Falk, L., 1994. A generalized mixing model for initial contacting of reactive fluids. *Chemical Engineering Science*, 49(24), pp.5127-5140.
- Xiao, Q., Lim, T.T. and Chew, Y.T., 2002. Second Taylor vortex flow: Effects of radius ratio and aspect ratio. *Physics of Fluids*, *14*(4), pp.1537-1539.
- Zhu, Q., Xiao, H., Zhang, R., Geng, S. and Huang, Q., 2019. Effect of impeller type on preparing spherical and dense Ni_{1-x-y}Co_xMn_y(OH)₂ precursor via continuous co-precipitation in pilot scale: A case of Ni_{0.6}Co_{0.2}Mn_{0.2} (OH)₂. *Electrochimica Acta*, *318*, pp.1-13.

CHAPTER 5

EFFECT OF HYDRODYNAMIC HETEROGENEITY ON PARTICLE DISPERSION IN A TAYLOR-COUETTE FLOW REACTOR WITH VARIABLE CONFIGURATIONS OF INNER CYLINDER

SUMMARY

Taylor vortex and its typical structure create the local hydrodynamic environment for particle preparation, and exert interfacial forces on particles. The observation of the dynamic interaction between Taylor vortices and the particles is meaningful for a better control of particle behaviour in the TC reactor. Therefore, the simulation of barium sulfate particle trajectories was carried out in this Chapter, taking the effect of hydrodynamic heterogeneity on particle dispersion in the CTC and LTC into consideration. The tracking of particle dispersion was based on the Euler-Lagrange approach, where the reactant solution phase was solved in the Eulerian reference frame, while the particle dispersion was calculated by tracking a large number of particles with consideration of the interfacial forces acting on the particles and adopting the actual particle properties measured from the particle synthesis experiments. The simulation reveals that particle dispersion is significantly enhanced by increasing the inner cylinder rotational speed, characterized by particle distribution for given the same particle residence time. Particle trajectories or dispersion are influenced by the turbulent Taylor vortices. Particle radial dispersion affects the particle classification by presenting different particle axial velocities in radial direction, while particle axial dispersion can be seen as an indicator of the global mixing occurring in the TC reactor, which is enhanced at high rotational speed, especially in the LTC. The calculated dispersion coefficient is found to distribute similar to the shape of particle size distribution based on the experimental results.

5.1 Introduction

The synthesis of fine particles are dependent on the dispersions of the primary particles. This can be achieved through the interaction between fluid flow and particles by the mass transfer mechanism with turbulent shear action to aggregate the particles to form larger clusters. During this procedure, particle properties are changed, being strongly dependent on the applied shear rate. In the literature, various studies exist addressing the effect of the shear intensity on particle size and shapes using different reactors (Serra *et al.*, 1997; Bubakova *et al.*, 2013; and Mayra and Kim, 2015). In these studies, the resulting particle populations are analysed by considering the volume average shear rate, $\langle G \rangle = \sqrt{\langle \varepsilon \rangle / \nu}$, obtained from the power input usually serves as the characteristic

quantity of the flow field. However, in reality for a given reactor, the shear rate exhibits a distinct distribution, which has a significant impact on the particle dispersion (Shen and Yeung, 1997; and Li *et al.*, 2019). As both aggregation and breakage of the particle in the dispersion are strongly dependent on the shear rate, the effect of the heterogeneity of the flow field inside the reactor on the particle dispersion needs to be considered.

Generation of the Taylor vortices is the most distinct feature in the TC reactor. They often appear in pairs in the gap area and vary due to the sensitivity to many influence factors, such as the reactant fluid property, inner cylinder geometry and rotational speed. Previous studies, for example, Snyder (1961); Lathrop et al. (1992) and Ehrl et al. (2010) among others have summarized a series of instabilities driven by the centrifugal force when the Reynolds number or Taylor number exceeds a critical value to yield Taylor vortices. The heterogeneity in the TC reactor will experience the flow pattern changes from Taylor vortex flow, wavy Taylor vortex flow, modulated wavy Taylor vortex flow, turbulent Taylor vortex flow to fully developed Taylor flow. Experimentally, Vaezi et al. (1997) have measured the intensity of turbulent velocity fluctuation in a TC reactor by means of Laser-Doppler velocimetry (LDV) and Wang et al. (2005) and Tokgoz et al. (2012) have adopted the particle image velocimetry (PIV) to measure the velocity field data. In the numerical simulation of the flow in the TC reactor, CFD modelling has been widely adopted to obtain the important information of the flow in the reactor, especially for the turbulence which has a dominant effect

on the particle dispersion. Such numerical simulations can be found, for example, by using the Reynolds stress model (Marchisio and Barresi, 2003; and Grossmann et al., 2014), and by employing the large eddy simulation (LES) (Bazilevs and Akkerman, 2010). For numerical modelling the particle dispersion in the TC reactor, Chouippe et al. (2014) has investigated the dispersion behaviour of bubbles in turbulent Taylor-Couette flow, revealing the phenomenon of the preference of bubble accumulation. Wang et al. (2005) used k- ε model coupled with PIV validation and the quadrature method of moments (QMOM), to predict the mean particle size of latex sphere under the effect of local fluid shear in turbulent Taylor-Couette flow. Dutta and Ray (2004) utilized the Taylor-Couette flow to realise water purification. As the Taylor-Couette flow has the feature of a narrow shear rate distribution, the application of such flow can facilitate the particle classification to acquire uniform particle size, so that the particle rheological behaviour and other properties can be changed accordingly. Also, when the density difference between the particles and the fluid is small, shear-induced particle migration under the influence of Taylor vortices will be beneficial to the classification of particle size (Kim et al., 2013). This is strongly associated with the dispersion of particles in the TC reactor. Ohmura et al. (2005) has successfully realized the classification of particles with various sizes using the TC reactor, validated by both numerical simulation and the actual experiments. They have observed that large particles, which are located near the edges of Taylor vortex, tend to be transported downward or upward due to the effect of outward and inward impinging jet flows formed in

the regions between the Taylor vortices while small particles are mainly remained in the core of vortices.

Taylor-Couette turbulent flow has been recognised as an effective way for the synthesis of various particles due to its shear controllable feature. Jung et al. (2010) prepared calcium carbonate (CaCO₃) particles using a TC reactor. The synthesised CaCO₃ agglomerates present various sizes and morphologies when changing the operating conditions such as reactant flow rate, concentration and angular velocity of inner cylinder. They also compared the particles synthesized using the TC reactor with those using a stirred tank. Interestingly, they reported that the adoption of TC reactor may be appropriate to obtain smaller size particles with a uniform shape due to rather homogenous mixing conditions available in such reactor. Nguyen et al. (2011, 2012) employed a TC crystallizer, working in a continuous mode with multiple feeding mode to obtain guanosine 5-monophosphate (GMP) crystals. They observed that the phase transformation of GMP in the TC crystallizer is about ten times faster than that in the conventional stirred tank crystallizer. They have attributed this phenomenon to the well control of the mass transfer rate and mean residence time in the TC crystallizer. In the fabrication of lithium ion batteries, the TC crystallizer can be seen as an effective device to synthesize precursors of cathode materials for lithium ion batteries, such as Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)₂ (Kim et al., 2011), and Ni_{0.9}Co_{0.05}Mn_{0.05}(OH)₂ according to Kim *et al.*'s series studies (Mayra and Kim, 2015; and Thai et al., 2015), and the most promising core-shell structure (Kim

and Kim, 2017). The synthesized secondary particles were found to exhibit good properties in terms of tap density, particle size, and morphology. It is deduced that under the effect of Taylor vortices, the exposure of agglomerates to local turbulence induced shear will be beneficial to spherical particle growth and formation of the dense structure.

It should be noted that these studies are mainly focused on the experimental preparation of particles and the interaction of turbulence and particles is not fully investigated. In order to explain the results of particle properties, they generally used the empirical correlations between the particle size and flow shear generated by Taylor vortices. So far, limited work has been conducted in relation to how the hydrodynamics, especially the turbulent flow field, in a TC reactor influences the particle formation and dispersion. Nemri *et al.* (2013) used Kalliroscope AQ-1000 flakes to observe flow pattern in the TC reactor, and the flake trajectory was used to observe the inter-vortex mixing, but their simulation was carried out with the single phase flow, and these particles were neutral particles without true attributes. We cautiously point out that it is the local hydrodynamics that provides the environment for particles to interact with the turbulent eddies, consequently bringing out the particle formation and growth. These mentioned studies lack the interpretation of the interaction

In the present work, we investigate the barium sulfate particle dispersion in the

TC reactor with variable configurations of inner cylinder, taking into account the momentum exchange between carrier fluid and barium sulfate particles. The properties of the particles are set similar to those obtained using the TC reactor from our previous experiment, including particle density, particle size, and its distribution (Liu et al., 2020). The parameters that influence the particle dispersion will be assessed, including the rotational speed (or characterized by the Reynolds number) and the configurations of the inner cylinder, where circular and lobed cross-sectional profiles are concerned. The flow field information is firstly obtained by CFD, then the tracking of particle trajectory will be realized by using Euler-Lagrange method (discrete phase model) with two-way coupling. This chapter will be organised as follows. Section 5.2 will present the theoretical background and modelling details for evaluating the fine particle dispersion in the TC reactor system, while Section 5.3 will present the results and discussion on the particle dispersion behaviour and the likely implication for synthesis of fine particles using the TC reactor and finally, Section 5.4 will summarise the conclusions derived from the study.

5.2 Mathematical modelling

The hydrodynamics in the TC reactor as used in the present study can be described by the existing two-phase flow model, which consists of a continuous liquid phase, the reactant solution here, and a certain amount of suspended particles, usually measured by the volume fraction. As the volume fraction of the dispersed particles in the experiments is smaller than 10%, the adoption of Eulerian-Lagrangian approach deems appropriately for description of particle dispersion in the synthesis process using the TC reactor. Also, the use of Lagrangian framework allows for the rigorous tracking of the movement of individual particles so that the dispersion can be well defined based on the statistics of the particle trajectories. In the meantime, the particle size distribution, which is important in determining particle characteristics, can be implemented into the numerical simulation, yielding a better prediction for particle dispersion (Marocco and Inzoli, 2009).

5.2.1 Governing equations

5.2.1.1 Liquid phase

As the effect of hydrodynamic heterogeneity on particle dispersion in the TC reactor is studied, the appropriate description of the interaction between continuous phase and discrete phase is crucial and two-way coupling has to be considered. Thus, the conservation equations for continuous phase are given by

Continuity equation:

$$\frac{\partial}{\partial t}(\alpha_L \rho_L) + \nabla \cdot (\alpha_L \rho_L \boldsymbol{u}_L) = -\dot{M}_{L-P}$$
(5.1)

Momentum conservation equation:

$$\frac{\partial}{\partial t}(\alpha_L \rho_L) + \nabla \cdot (\alpha_L \rho_L \boldsymbol{u}_L \boldsymbol{u}_L) = -\alpha_L \nabla p + \nabla \cdot (\alpha_L \tau_L) + \alpha_L \rho_L \boldsymbol{g} + \boldsymbol{F}_{P-L} - \dot{\boldsymbol{M}}_{L-P} \boldsymbol{u}_L$$
(5.2)

where u_L is the Reynolds-average velocity, ρ_L is the liquid density, p is the static pressure, τ_L is the stress tensor, $\rho_L g$ is the gravitational force, and F_{P-L} is the forces acting on the liquid phase due to the particles, which arises from the interaction with the dispersed particles. \dot{M}_{L-P} denotes the mass transfer occurring between the reactant liquid and the particles. As the particle size concerned compared with the turbulent eddies is small, this interfacial mass transfer has been neglected in the present work.

In order to determine the flow pattern in the TC reactor, a Reynolds number has been defined, expressed as

$$Re = \frac{\omega_i r_i d}{\nu} \tag{5.3}$$

where ω_i and r_i are the angular velocity and the radius of the inner cylinder, respectively. For the LTC, r_i will be replaced by the equivalent or hydraulic radius of the inner cylinder. *d* is the gap size, and *v* is the kinematic viscosity of fluid. The minimum rotational speed used is 300 rpm, corresponding to the Reynolds number of 12384. Thus, it would be safe to employ the RNG *k*- ε

turbulence model in the simulation as the flow in the TC reactor has the feature of swirling. However, the entrained particles by Taylor vortices will have the impact on the reactant liquid turbulent kinetic energy and turbulent energy dissipation rate distribution. Such effect has been considered by adding the source terms into the RNG k- ε model. When the volume fraction of the dispersed particles is very small, turbulence modulation by dispersed phase is weak. In such case, the RNG k- ε equations can be simplified and their original forms without including source terms are adopted.

k equation:

$$\frac{\partial}{\partial t}(\rho k) + \nabla \cdot (\rho k \boldsymbol{u}_L) = \nabla \cdot \left(\frac{\mu_{eff}}{\sigma_k} \nabla k\right) + G_k - \rho \varepsilon$$
(5.4)

 ε equation:

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\varepsilon \boldsymbol{u}_L) = \nabla \cdot \left(\frac{\mu_{eff}}{\sigma_{\varepsilon}}\nabla\varepsilon\right) + C_{1\varepsilon}\frac{\varepsilon}{k}G_k - C_{2\varepsilon}\rho\frac{\varepsilon^2}{k} - R_{\varepsilon} \quad (5.5)$$

As our previous study has simulated the flow field for single phase flow in the TC reactor with the same configuration and operating conditions, the definition of these terms or functions in the right hand side of both equations can be referred to Liu *et al.* (2020).

5.2.1.2 Dispersed phase

The dispersed particle tracking is conducted in a Lagrangian reference frame, where individual particle trajectories can be tracked by solving the particle equation of motion. The particles are divided into several particle parcels according to the experimentally obtained particle size distribution. The positions of particles can be obtained from the following equation:

$$\frac{dx_p}{dt} = \boldsymbol{u}_p \tag{5.6}$$

The velocity of particles, u_p can be obtained by solving the force balance equation:

$$\frac{d\boldsymbol{u}_p}{dt} = F_D(\boldsymbol{u}_L - \boldsymbol{u}_p) + F_L(\boldsymbol{u}_L - \boldsymbol{u}_p) + \frac{g(\rho_p - \rho_L)}{\rho_p}$$
(5.7)

where ρ_p is the density of particles. As the density of barium sulfate particles (4500 kg/m³) is larger than that of the reactant liquid, the drag force will be dominant and the added mass force is ignored. The lift force is still considered as the particles are subjected to strong shear induced by the Taylor vortices and embedded turbulent eddies in the TC reactor. The drag force factor F_D can be estimated using Equation (5.8)

$$F_D = \frac{18\mu}{\rho_p d_p^2} \frac{C_D R e_p}{24}$$
(5.8)

where μ is the liquid viscosity, C_D is the drag coefficient, d_p is the particle

diameter, and Re_p is the Reynolds number based on the particle diameter, given by

$$Re_p = \frac{\rho d_p |\boldsymbol{u}_p - \boldsymbol{u}_L|}{\mu} \tag{5.9}$$

It is assumed that barium sulfate particles can be still treated as smooth spherical particles. Then, the drag coefficient, C_D can be estimated using the following expression,

$$C_D = a_1 + \frac{a_2}{Re_p} + \frac{a_3}{Re_p^2}$$
(5.10)

where a_1 , a_2 , and a_3 are constants, depending on the value of Re_p . Details can refer Morsi and Alexander (1972). With respect to the lift force factor, the Saffman's lift force model is adopted, given by

$$F_L = \frac{2K\nu^{1/2}\rho d_{ij}}{\rho_p d_p (d_{lk}d_{kl})^{1/4}}$$
(5.11)

where *K* is a constant, equal to 2.594, and d_{ij} is the deformation tensor. Equation (5.7) is the ordinary differential equation for description of movement of individual particles and can be solved by integration over discrete time steps, yielding the predicted particle trajectories. It should be noted that the time step taken in the integration should be smaller than the typical turbulence integral time scale for turbulent eddies in the TC reactor. During the calculation, the

thumb rule used for modelling the continuous phase is that the time step used for transient simulation is 10 times greater than that for the dispersed particle tracking, ensuring the sufficient interaction between the turbulent eddies and the particles. In order to catch up the effect of turbulence on the particle dispersion, stochastic tracking model is employed. Because this model takes the instantaneous turbulent velocity fluctuation, u'_L at the location of the particle, the instantaneous velocity for the continuous phase at the position of the particle is given by

$$\boldsymbol{u}_L = \overline{\boldsymbol{u}_L} + \boldsymbol{u}_L' \tag{5.12}$$

Since the turbulent kinetic energy at the position of the particle in the flow can be obtained, the root mean square value of each fluctuating component u'_L can be approximated by

$$\sqrt{\overline{u_L'^2}} = \sqrt{\overline{v_L'^2}} = \sqrt{\overline{w_L'^2}} = \sqrt{2k/3}$$
 (5.13)

5.2.1.3 Momentum source term

Momentum is exchanged during the interaction of continuous phase and discrete phase. The momentum source term arises from the forces exerting on individual particles. As it has been indicated above, drag force, and lift force are dominant forces for the currently investigation system, therefore, the momentum exchange can be expressed by the following equation,

$$\boldsymbol{F}_{P-L} = \sum \left[\frac{18\mu}{\rho_p d_p^2} \frac{C_D R e_p}{24} \left(\boldsymbol{u}_L - \boldsymbol{u}_p \right) + \frac{2K\nu^{1/2}\rho d_{ij}}{\rho_p d_p (d_{lk} d_{kl})^{1/4}} \left(\boldsymbol{u}_L - \boldsymbol{u}_p \right) \right] \dot{\boldsymbol{m}}_p \Delta t \quad (5.14)$$

where \dot{m}_p is the mass flow rate of particles.

5.2.2 Particle size distribution

In the previous study (Liu *et al.*, 2020), the particle size and its distribution have been obtained by using Malvern Mastersizer. These experimental data of particle size distributions at different Reynolds numbers are directly used in the particle inlet. During the calculation, the particle size distribution is assumed to follow the Rosin-Rammler distribution, where the mass fraction of those particles, whose diameter is greater than d_p is given by

$$Y_d = e^{-(d_p/d_p)^n} (5.15)$$

where Y_d is the accumulated mass fraction for particles with the diameter greater than d_p , \bar{d}_p is the size constant, and *n* is the size spread parameter. Once the particle size is classified into several discrete diameter groups, the mass fraction of each group can be obtained accordingly. In order to determine the values of parameter *n*, and \bar{d}_p , Equation (5.15) can be converted to a linear format by taking the logarithm operation for both sides of the equation, yielding

$$ln(-lnY_d) = nlnd_p - nln\bar{d}_p \tag{5.16}$$

Based on the fitted straight line, the value of n can be obtained from the slope while the value of \bar{d}_p can be obtained from the intercept.

5.2.3 Initial and boundary conditions

For the continuous phase, the inlet and outlet boundary conditions were set as the velocity inlet and pressure outlet, respectively. Hydraulic diameter was specified while the turbulent intensity was assumed to be equal to 5%, assuming the feeding to be smooth. No-slip boundary conditions were imposed to all the inner cylinder and outer cylinder surfaces and the standard wall functions were applied to the meshes close to the inner and outer cylinder surfaces.

For the discrete phase, the particle parcels were injected from the inlet surface, where the total flow rate for all particles was set based on the actual experimental results (Liu *et al.*, 2020). The collision between the particles and the surfaces of the cylinder is assumed to be elastic, which can be specified as the reflect type of boundary condition. The escape boundary condition was assigned for the particle inlet and outlet to eliminate those unphysical particle trajectories, indicating that the particles encountering the boundaries will not be accounted in the simulation and their trajectory calculations will be terminated.

5.2.4 Physical TC reactor model

The configuration of the TC reactor is depicted in Figure 5.1 (a), and its dimensions are listed in Table 5.1. Based on the previous study of the preparation of barium sulfate particle (Liu *et al.*, 2020), it has been demonstrated that a modified geometry of inner cylinder from the traditional CTC to the LTC can effectively intensify the local turbulence, beneficial to the particle aggregation. Therefore, the present simulations focus on the flow in the LTC at different rotational speeds. For comparison purpose, the simulation on particle dispersion at a high rotational speed of 1000 rpm in the CTC is also conducted, and the computational domain is shown in Figure 5.2. Procedures of the preparation of barium sulfate particles can be found in the study of Liu *et al.* (2020).



Figure 5.1 (a) Configuration of the TC reactor; and (b) Inner cylinder geometry

for the: (i) CTC; and (ii) LTC.



Figure 5.2 Mesh setup for computational domain: (a) global mesh view; and (b) mesh refinement for inner fluid zone.

Table 5.1 Dimensions and operating conditions of the TC reactor

Dimension	CTC	LTC
Reactor length, L (mm)	300.00	300.00
Inner cylinder radius, r_i (mm)	40.00	40.19
Outer cylinder radius, r_o (mm)	50.00	50.00
Gap size, <i>d</i> (mm)	10.00	9.81
Rotational speed, Ω (rpm)	300, 600, 800, 1000	1000

5.2.5 Numerical simulation

The commercial CFD software, Fluent 17.0, was employed to simulate the particle dispersion in the Taylor-Couette flows. The flow and hydrodynamic heterogeneity were described by solving the Reynolds-Average Navier-Stokes equations coupled with RNG k- ε model. Meanwhile, the particles were tracked using equation of motion as defined by Equation (5.7). Computational mesh was created by ANSYS ICEM with a total cell number more than 1,100,000. According to the dimensions of the TC reactor as listed in Table 5.1, a mesh setup with 147×48×16 (circumferential×axial×radial) was adopted in the numerical simulation, as illustrated in Figure 5.2. For the inner fluid zone containing lobed inner cylinder, the mesh has been further refined, as shown in Figure 5.2 (b). The simulation details can be found in Liu et al. (2020). The pressure-velocity coupling was realized by SIMPLEC algorithm while PRESTO! Scheme was used for the pressure calculation. The second-order upwind scheme was adopted for the calculation of momentum, and the same for the calculation of turbulent kinetic energy and turbulent energy dissipation. From the trial simulation, the time step size for continuous liquid phase was set at 10^{-3} s as the Taylor vortices can be still well captured from the simulation. The particles were tracked using a time step of 10^{-4} s. The convergence criteria for all parameters were set 10^{-3} in relative scaling.

5.3 Results and discussion
5.3.1 Characterisation of particle entrainment by Taylor vortices

Under the condition of a certain Reynolds number, Taylor vortices are generated in the TC reactor, where the two adjacent vortices are counter-rotating, embedded various scales of turbulent eddies from large to Kolmogorov dissipation scale. Also, the inward and outward impinging jet flows between the two vortices are created (Li et al., 2015). Figure 5.3 shows the distribution of particles in the gap of the LTC on the conditions of various rotational speeds for given the same particle residence time. Colour bar denotes particle velocity magnitude. It can be seen clearly from the figure that with increase of the rotational speed, particles are entrained and dispersed in intra-vortices. It has been shown that the radial velocity gradient in the inward or outward impinging jet flows will increases when the inner cylinder running at high rotational speed (Liu et al., 2020). Such increased radial velocity gradient will intensify the particle movement around the Taylor vortices, pushing the particles accumulating in the stagnation zones formed close to either the inner surface of the outer cylinder or the outer surface of the inner cylinder. However, the axial transport of the Taylor vortices will bring out the enhanced dispersion of particles across the vortices while interacting with the embedded turbulent eddies. Although the density of barium sulfate is greater than the reactant liquid, the particle size is extremely small with the order of 10^{-7} m. This results in particles to be easily suspended throughout the entire reactor as can be observed from Figure 5.3, especially when the LTC is working at a high rotational speed.

For the given residence time, the simulation results show that the particles have not yet dispersed to across the reactor length at a rotational speed of 300 rpm while the number of particles have been entrained to the top of the reactor at the rotational speed exceeding 800 rpm. This clearly indicates that the turbulence shear enhanced by increasing the inner cylinder of the LTC has a significant impact on particle dispersion. It can be also observed from Figures 5.3 (c) and (d) that the particles with high velocity magnitude tend to distribute in the large gap regions in the LTC when working at high rotational speed. This is very likely to attribute to the fact that the impinging jet flows formed between the two deformed Taylor vortices strongly entrain the particles towards these regions. Also, the flow in circumferential direction experiences an expansion following by a contraction due to the gradually decrease gap for the LTC. Figure 5.3 (e) displays the particle distribution in the CTC for comparison, which shows the dispersion of particles in the CTC is more even than that in the LTC for operating the same rotational speed. Obviously, due to the axisymmetric feature of the CTC and the uniformly distributed radial circumferential velocity gradient, the external forces exerted on the particles ensure that particles are dispersed relatively uniform in the circumferential direction. In contrast, the radial circumferential velocity gradient in the LTC will experience the periodic change due to the deformed Taylor-vortices, thus causing the particles to disperse towards the large gap regions.



Figure 5.3 Particle distribution in the LTC: (a) 300 rpm; (b) 600 rpm; (c) 800 rpm; (d) 1000 rpm, and the CTC: (e) 1000 rpm.

5.3.2 Particle trajectory

In order to observe the interaction of particles with Taylor vortex, particles are tracked at a specified time interval. Figure 5.4 illustrates the predicted particle trajectory for the inner cylinder operating at 1000 rpm in the CTC and LTC, respectively. Here three trajectory paths are randomly selected for each reactor,

and the colour bar denotes the velocity magnitude of the flow field. Firstly, it can be seen from the streamlines created along the vertical cutting plane that the velocity magnitude is enhanced in the large gap region for the LTC in comparison to the CTC, consistent with the argument of Soos *et al.* (2017) that the heterogeneity in the TC reactor can be improved by varying the configuration of the inner cylinder. The main advantage of the LTC is that Taylor-Couette flow are still remained but the low velocity regions are reduced. Secondly, the particles injected from the inlet are entrained by Taylor vortices, and strongly interact with the embedded eddies. As a result, the particles are subsequently dispersed to follow a helical movement behaviour. The local amplified images with the arrow line clearly indicates the direction of particle entrainment.



Figure 5.4 Particle trajectory at 1000 rpm in the: (a) CTC; (b) amplification of the CTC; (c) LTC; and (d) amplification of the LTC.

It can be seen from Figure 5.5 that the low static pressure takes place at the outward impinging jet region between two adjacent Taylor vortices. However, it is contradicted with the expectation that the particles do not significantly accumulate in this region. This is likely caused by the change of dominating force in the gap of the TC reactor. In Qiao *et al.*'s (2005) study, they observed that light particles are easy to be trapped on the wall of the inner cylinder. Along the radial direction, the pressure force exerted on the particles is 6 times greater than the centrifugal force at low Reynolds numbers, which favourably drives the particles migrating towards the inner cylinder surface. With the increase in the Reynolds number, the drag force exerted on the particles. For heavy particles, their study found that they are trapped in the regions around the inner cylinder. This phenomenon can be interpreted by discussing the trapping of particles by Taylor vortices through the characterization using the Stokes number, defined by

$$St_{\eta} = \frac{\tau_p}{\tau_f} \tag{5.17}$$

where τ_p is the particle relaxation time, and τ_f is the characteristic time of the local flow of Kolmogorov scale turbulent eddies. τ_p and τ_f can be estimated by the following equations

$$\tau_p = \frac{\rho_p d_p^2}{18\mu} \tag{5.18}$$

$$\tau_f = \sqrt{\frac{\nu}{\varepsilon}} \tag{5.19}$$

As suggested by Crowe *et al.* (1997), if St < 1.0, particles will closely follow the fluid flow. In the present study, this indicates that the particles are entrapped by turbulent eddies embedded in the Taylor vortices and strongly interact with the eddies. On the contrary, if $St_{\eta}>1.0$, particles are dominated by their movement inertia, and they cannot respond immediately to the change of turbulent eddies. Figure 5.6 shows the Stokes number at different rotational speeds by using the average particle size obtained from the experimental results under the respective condition (Liu *et al.*, 2020). It can be seen clearly that at all the range of rotational speeds, the Stokes number, St_{η} , has the order of 10^{-4} , indicating the entrapment of particles by the turbulent eddies, being consistent with the observation of the particle trajectories as shown in Figure 5.4.



Figure 5.5 Pressure distribution at 1000 rpm in the: (a) CTC; and (b) LTC.



Figure 5.6 Stokes number at different Reynold numbers.

5.3.3 Particle dispersion in radial direction

As can be seen from the aforementioned results, particle trajectories are influenced by Taylor vortices in the TC reactor. In order to observe the particle dispersion in radial direction, a horizontal cutting plane was created, as displayed in Figure 5.7. Colour bar denotes the axial velocity magnitude of the particles. It can be seen from the figure that with increase of the rotational speed, the downward and upward velocity of the vortices will increase. Secondly, the particles with low slip velocity tend to distribute near the core of vortices while those with high slip velocity distribute near the wall of either inner cylinder or outer cylinder. It seems that there exists a separation strap of the particles inside and outside the vortices. The change of particle axial velocity component in radial direction is shown in Figure 5.8, which is quantitatively consistent with the results as shown in Figure 5.7. One can argue that when the particles are entrapped in the core of the vortices, they are mainly affected by the vortices and the embedded turbulent eddies. Thus, the dispersion will mainly occur in the vortices. It is interesting to note here that in Figure 5.8, when comparing the vector marked by green line (i.e., the axial velocity in small gap) with the one marked by blue line (i.e., axial velocity in large gap), high axial velocity is found to occur at the region with small gap near the inner cylinder. However, the results shown in Figure 5.3 suggest that velocity magnitude is relatively high in the region with the large gap. This may be the consequence of the circumferential flow passing the narrowest gap between the rotating inner

cylinder and the outer cylinder, generating a local circulation eddy which may generate a low pressure zone with high local velocity, as shown in Figure 5.5. Subsequently, the drag force increases as the result of the increase in slip velocity between the particle and local reactant liquid. This results have the implication that the LTC can be effective for particle classification. Actually, in the study of Kim *et al.* (2013), they investigated particle movement with a constant density of 1760 kg/m³ in a TC reactor, and they have found that large particles with the size up to 0.7 mm sink to the bottom through bypass flow while small particles (at least 0.05 mm) stay trapped in the core. In the study of Ohmura *et al.*'s (2005), they observed that large particles concentrate near the edges of vortex. However, for particle classification, not only particle size but also particle density plus local particle concentration should be taken into account. These joint factors should be further studied with the loading capacity of Taylor vortices by introducing the Stokes loading factor (Pomle *et al.*, 2007).



Figure 5.7 Particle distribution in terms of axial velocity in horizontal cutting plane of the LTC: (a) 300 rpm; (b) 600 rpm; (c) 800 rpm; (d) 1000 rpm, and the CTC: (e) 1000 rpm.



Figure 5.8 Axial velocity along radial position at: (a) 300 rpm; (b) 600 rpm; (c) 800 rpm; and (d) 1000 rpm.

5.3.4 Particle dispersion in axial direction

Figure 5.9 shows the scattered particle axial positions varying with time. At the rotational speed of 300 rpm, the time required to reach the farthest axial position measured from the bottom of the LTC is greater than 38 s, while when

increasing the rotational speed, less time is needed for the particles to disperse to the same distance. It can be seen from the figure that the time reduces to 21 s in the LTC at the rotational speed at 1000 rpm while the time is only 18 s in the CTC. This indicates that the deformed Taylor vortices in the LTC may have a stronger impact on the particle dispersion than those in the CTC. However, it is interesting to note that the particle dispersion fluctuation in the LTC is more apparent than that in the CTC, indicating that the particle dispersion is locally stochastic, and turbulent eddies fails to interact well with those particles.



Figure 5.9 Particle axial dispersed position.

In order to quantitatively estimate particle dispersion in the axial direction, an "effective particle diffusion coefficient" is used as suggested by Rudman (1998). It should be pointed out that this coefficient can also indicate the global mixing performance. In the experiment of Liu *et al.* (2020), the TC reactor was aligned vertically, and the particles were entrained in the axial direction by the Taylor

vortices formed in the reactor. Thus, the axial diffusion is appropriate to characterize global mixing. In order to ensure for a reliable estimation of the particle axial dispersion, a large number of particles should be tracked. In this study, more than 1,000 particles (parcels) were injected in the computational domain, whose trajectories were tracked based on the modelling as described in Section 5.2. The particle axial dispersion is thus calculated using Equation (5.20), given by

$$D_{z} = \lim_{t \to \infty} \frac{1}{N} \sum \frac{(z_{i}(t) - z_{i}(0))^{2}}{2t}$$
(5.20)

where Dz is the diffusion coefficient, N is the total number of particles tracked, $z_i(0)$ is the initial position of particles, and $z_i(t)$ is the axial position of the i^{th} particle at time step t.

Figure 5.10 (a) shows the axial diffusion coefficient as the function of time. Also, the particle size distribution at each condition are displayed for reference. As particles are entrained away from their initial position, D_z increases first, following by a dropping down, and then level off with time. By observing the results of particle size distribution, it can be seen that the uniform particle size with a narrower size distribution is achieved in the LTC at high rotational speed. However, in the CTC, particles size shows a rather broad size distribution, implying that the more time is taken for the particles to interact with the Taylor vortices, corresponding to the greater fluctuation of dispersion coefficient.

Some previous studies have investigated the relationship between the axial dispersion and the Reynolds number. Moore and Cooney (1995) suggested that for the wavy vortex flow, Dz is proportional to $Re^{1.05}$. Rudman (1998) found that for the modulated wavy vortex flow, Dz is proportional to Re, while Tam and Swinney (1987) indicated that for turbulent flow in the Taylor-Couette system, D_z is proportional to Re^{β} , where β is mainly dependent on the radius ratio. It can be seen that D_z will change non-monotonically with Re for different flow patterns in the TC reactor. For our study, the relationship between D_z and Re is illustrated in Figure 5.10 (b), which is consistent with those aforementioned studies, the diffusion coefficient increases with the increase of Reynolds number but the value of the coefficient for the CTC is smaller than that in the LTC. It should be noted that the average particle size obtained shows an opposite trend with the respect to the diffusion coefficient. As Dz can serve as an indicator of global mixing, the good mixing condition is achieved at high rotational speed, especially in the LTC. Thus, the use of the LTC can improve the particle synthesis process, as indicated by the greater D_z and being consistent with the previous study of Nemri et al. (2016). They indicated the existence of two types of mixing in the TC reactor, inter-vortex mixing and intra-vortex mixing. Inter-vortex mixing depends on the local turbulence and vortices such as the local impinging jet flows while intra-vortex mixing is dominated by the embedded turbulent eddies. An effective dispersion behaviour will create a good mixing condition for chemical reaction, intensifying particle preparation process.



Figure 5.10 (a) Diffusion coefficient distribution and particle size distribution; and (b) Diffusion coefficient and particle size at different Reynolds numbers.

It should be noted that particle size not only depends on the synthesis reaction condition but also the formed particles are influenced by shear force exerted on particle surface. Figure 5.11 shows the shear strain rate distribution along the middle vertical line in the gap, and this line is across the centres of all the Taylor vortices in the TC reactor. The blue line represents the large gap region, and the green line denotes the small gap region in the LTC. The maximum shear strain rate appears at the inward and outward impinging jet regions. Also, vortex induced shear increases with increase in the rotational speed. Although the shear strain rate in the CTC is distributed more evenly than that in the LTC, the volume-average shear strain rate in the CTC is much smaller than that in the LTC. This indicates that the alteration of the cross-sectional profile of inner cylinder can effectively enhance the turbulence eddy induced shear. Due to the periodic variation of gap size in the LTC, turbulence intensification can be obtained, resulting in the generation of more turbulent eddies. Consequently, such turbulent shear acts on particles, curbing the particle growth so as to control the particle size.



Figure 5.11 Shear strain rate along axial position at: (a) 300 rpm; (b) 600 rpm; (c) 800 rpm; and (d) 1000 rpm.

5.4 Conclusions

Effect of hydrodynamic heterogeneity on particle dispersion in TC reactors with variable configurations of inner cylinder has been investigated using CFD modelling. Tracking of particle motion was based on the Euler-Lagrange approach, where the reactant solution phase was solved in the Eulerian reference frame, while the particle dispersion was calculated by tracking a large number of barium sulfate particle with consideration of the interfacial forces acting on the particles and adopting the actual particle properties of particles measured

from particle synthesis experiments. The main observations and results are summarized as follows:

(1) The simulation reveals that particle dispersion is significantly enhanced by increasing the inner cylinder rotational speed, characterized by particle distribution for given the same particle residence time. Particles with high velocity magnitude tend to distribute in the large gap regions in the LTC, likely being attributed to the entrainment of particles by the impinging jet flows towards these regions, and the gradually decrease gap for the LTC, where the flow in circumferential experiences an expansion following by a contraction. The calculated particle trajectories in both the LTC and CLC exhibit helical movements, entrapped by Taylor vortices when judging by the Stokes number.

(2) Particle dispersion in radial direction affects the particle classification by presenting different particle axial velocities. It indicates that there exists a separation strap of the particles inside and outside the vortices. Such axial velocity distribution may be due to the circumferential flow, generating local circulation eddies.

(3) Particle dispersion in axial direction, which can be seen as an indicator of the global mixing occurring in the TC reactor, has also been investigated. The axial dispersion coefficient D_z was numerically calculated from Lagrangian tracking simulation, revealing a significant impact of the local turbulent

impinging jet flows around the Taylor vortices on the mixing. The greater diffusion coefficient indicating a good mixing condition is achieved at high rotational speed, especially in the LTC. The distribution of the calculated dispersion coefficient is found to be similar to the shape of particle size distribution based on the experimental results (Liu *et al.*, 2020). The local shear strain rate enhancement due to the inner cylinder cross-sectional profile modification, and the generation of more turbulent eddies due to the periodic variation of gap size in the LTC acting on particles are beneficial to the formation of uniformly small particles.

References

- Bazilevs, Y. and Akkerman, I., 2010. Large eddy simulation of turbulent Taylor–Couette flow using isogeometric analysis and the residual-based variational multiscale method. *Journal of Computational Physics*, 229(9), pp.3402-3414.
- Bubakova, P., Pivokonsky, M. and Filip, P., 2013. Effect of shear rate on aggregate size and structure in the process of aggregation and at steady state. *Powder Technology*, 235, pp.540-549.
- Chouippe, A., Climent, E., Legendre, D. and Gabillet, C., 2014. Numerical simulation of bubble dispersion in turbulent Taylor-Couette flow. *Physics of Fluids*, 26(4), p.043304.
- Coufort, C., Bouyer, D. and Liné, A., 2005. Flocculation related to local hydrodynamics in a Taylor–Couette reactor and in a jar. *Chemical Engineering Science*, 60(8-9), pp.2179-2192.
- Crowe, C.T., Troutt, T.R. and Chung, J.N., 1996. Numerical models for twophase turbulent flows. *Annual Review of Fluid Mechanics*, 28(1), pp.11-43.
- Dutta, P.K. and Ray, A.K., 2004. Experimental investigation of Taylor vortex photocatalytic reactor for water purification. *Chemical Engineering Science*, *59*(22-23), pp.5249-5259.
- Ehrl, L., Soos, M., Wu, H. and Morbidelli, M., 2010. Effect of flow field heterogeneity in coagulators on aggregate size and structure. *AIChE Journal*, *56*(10), pp.2573-2587.

- Grossmann, S., Lohse, D. and Sun, C., 2014. Velocity profiles in strongly turbulent Taylor-Couette flow. *Physics of Fluids*, *26*(2), p.025114.
- Grossmann, S., Lohse, D. and Sun, C., 2016. High–reynolds number taylorcouette turbulence. *Annual Review of Fluid Mechanics*, 48, pp.53-80.
- Jung, W.M., Kang, S.H., Kim, K.S., Kim, W.S. and Choi, C.K., 2010. Precipitation of calcium carbonate particles by gas–liquid reaction: Morphology and size distribution of particles in Couette-Taylor and stirred tank reactors. *Journal of Crystal Growth*, *312*(22), pp.3331-3339.
- Kantoush, S.A., De Cesare, G., Boillat, J.L. and Schleiss, A.J., 2008. Flow field investigation in a rectangular shallow reservoir using UVP, LSPIV and numerical modelling. *Flow Measurement and Instrumentation*, *19*(3-4), pp.139-144.
- Kim, J.M., Chang, S.M., Chang, J.H. and Kim, W.S., 2011. Agglomeration of nickel/cobalt/manganese hydroxide crystals in Couette–Taylor crystallizer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384(1-3), pp.31-39.
- Kim, J.S., Kim, D.H., Gu, B. and Yang, D.R., 2013. Simulation of Taylor– Couette reactor for particle classification using CFD. *Journal of Crystal Growth*, 373, pp.106-110.
- Kim, J.E. and Kim, W.S., 2017. Synthesis of Core–Shell Particles of Nickel– Manganese–Cobalt Hydroxides in a Continuous Couette-Taylor Crystallizer. *Crystal Growth & Design*, 17(7), pp.3677-3686.

Lathrop, D.P., Fineberg, J. and Swinney, H.L., 1992. Transition to shear-driven

turbulence in Couette-Taylor flow. Physical Review A, 46(10), p.6390.

- Li, G., Yang, X. and Ye, H., 2015. CFD simulation of shear flow and mixing in a Taylor–Couette reactor with variable cross-section inner cylinders. *Powder Technology*, 280, pp.53-66.
- Li, J., Zeng, X.A., Brennan, C.S. and Chen, X.D., 2019. Micron-size lactose manufactured under high shear and its dispersion efficiency as carrier for Salbutamol Sulphate. *Powder Technology*, 358, pp.39-45.
- Liu, L., Yang, X., Li, G., Huang, X. and Xue, C., 2020. Shear controllable synthesis of barium sulfate particles using lobed inner cylinder Taylor-Couette flow reactor. *Advanced Powder Technology*, 31(3), pp.1088-1099.
- Marchisio, D.L. and Barresi, A.A., 2003. CFD simulation of mixing and reaction: the relevance of the micro-mixing model. *Chemical Engineering Science*, *58*(16), pp.3579-3587.
- Marocco, L. and Inzoli, F., 2009. Multiphase Euler–Lagrange CFD simulation applied to wet flue gas desulphurisation technology. *International Journal of Multiphase Flow*, *35*(2), pp.185-194.
- Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-Rich hydroxide in reaction crystallization: Effect of Taylor vortex dimension and intensity. *Crystal Growth & Design*, *15*(4), pp.1726-1734.
- Moore, C.M. and Cooney, C.L., 1995. Axial dispersion in Taylor-Couette flow. *AIChE Journal*, *41*(3), pp.723-727.
- Morsi, S.A.J. and Alexander, A.J., 1972. An investigation of particle trajectories in two-phase flow systems. *Journal of Fluid mechanics*, *55*(2), pp.193-208.

- Nemri, M., Climent, E., Charton, S., Lanoe, J.Y. and Ode, D., 2013. Experimental and numerical investigation on mixing and axial dispersion in Taylor–Couette flow patterns. *Chemical Engineering Research and Design*, 91(12), pp.2346-2354.
- Nemri, M., Charton, S. and Climent, É., 2016. Mixing and axial dispersion in Taylor–Couette flows: the effect of the flow regime. *Chemical Engineering Science*, 139, pp.109-124.
- Nguyen, A.T., Kim, J.M., Chang, S.M. and Kim, W.S., 2011. Phase Transformation of Guanosine 5-Monophosphate in Continuous Couette– Taylor Crystallizer: Experiments and Numerical Modeling for Kinetics. *Industrial & Engineering Chemistry Research*, *50*(6), pp.3483-3493.
- Nguyen, A.T., Joo, Y.L. and Kim, W.S., 2012. Multiple feeding strategy for phase transformation of GMP in continuous Couette–Taylor crystallizer. *Crystal Growth & Design*, *12*(6), pp.2780-2788.
- Ohmura, N., Suemasu, T. and Asamura, Y., 2005. Particle classification in Taylor vortex flow with an axial flow. In *Journal of Physics: Conference Series* (Vol. 14, No. 1, p. 64). IOP Publishing.
- Qiao, J., Deng, R. and Wang, C.H., 2015. Particle motion in a Taylor vortex. *International Journal of Multiphase Flow*, 77, pp.120-130.
- Rudman, M., 1998. Mixing and particle dispersion in the wavy vortex regime of Taylor–Couette flow. *AIChE Journal*, *44*(5), pp.1015-1026.

Serra, T., Colomer, J. and Casamitjana, X., 1997. Aggregation and breakup of

particles in a shear flow. *Journal of Colloid and Interface Science*, *187*(2), pp.466-473.

- Shen, P. and Yeung, P.K., 1997. Fluid particle dispersion in homogeneous turbulent shear flow. *Physics of Fluids*, *9*(11), pp.3472-3484.
- Snyder, H.A., 1962. Experiments on the stability of spiral flow at low axial Reynolds numbers. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 265(1321), pp.198-214.
- Soos, M., Wu, H. and Morbidelli, M., 2007. Taylor-Couette unit with a lobed inner cylinder cross section. *AIChE Journal*, *53*(5), pp.1109-1120.
- Tam, W.Y. and Swinney, H.L., 1987. Mass transport in turbulent Couette-Taylor flow. *Physical Review A*, *36*(3), p.1374.
- Tarpagkou, R. and Pantokratoras, A., 2013. CFD methodology for sedimentation tanks: The effect of secondary phase on fluid phase using DPM coupled calculations. *Applied Mathematical Modelling*, 37(5), pp.3478-3494.
- Thai, D.K., Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of ni-rich hydroxide crystals in taylor vortex flow. *Powder Technology*, 274, pp.5-13.
- Tokgoz, S., Elsinga, G.E., Delfos, R. and Westerweel, J., 2012. Spatial resolution and dissipation rate estimation in Taylor--Couette flow for tomographic PIV. *Experiments in Fluids*, *53*(3), pp.561-583.
- Vaezi, V., Oh, E.S. and Aldredge, R.C., 1997. High-intensity turbulence measurements in a Taylor-Couette flow reactor. *Experimental Thermal and Fluid Science*, 15(4), pp.424-431.

Wang, L., Vigil, R.D. and Fox, R.O., 2005. CFD simulation of shear-induced aggregation and breakage in turbulent Taylor–Couette flow. *Journal of Colloid and Interface Science*, 285(1), pp.167-178.Wang, L., Olsen, M.G. and Vigil, R.D., 2005. Reappearance of azimuthal waves in turbulent Taylor–Couette flow at large aspect ratio. *Chemical Engineering Science*, 60(20), pp.5555-5568.

CHAPTER 6

MODELLING OF TURBULENT SHEAR CONTROLLABLE CO-PRECIPITATION SYNTHESIS OF LITHIUM ION BATTERY CATHODE PRECURSOR MICRO-PARTICLES IN A TAYLOR-COUETTE FLOW REACTOR WITH VARIABLE CONFIGURATIONS OF INNER CYLINDER

SUMMARY

From previous fundamental study of barium sulfate particles synthesized in the TC reactor, it is found that such device is promising in terms of process intensification and particle property control, thereby having wide applications to the preparation of various particles. Firstly, the relatively homogenous hydrodynamic condition in such TC reactor system is favourable for the formation of spherical particles. Different from traditional reactors, the vortices are evenly distributed along the axial direction in the TC reactor with the same length scale. Accordingly, turbulence induced eddies down to the particle length scale are recognised to be isotropic. Thus, eddy shear can evenly act on particle surface, facilitating particles to become spherical. Secondly, the scale of these turbulent eddies can be easily controlled by adjusting operating parameters, such as rotational speed, and axial velocity. Accordingly, the eddy capacity to load particles can be adjusted. As agglomeration of primary particles results in the formation of secondary particles, which takes place within eddies, eddies can be suggested to play a critical role in determining final particle compactness.

Based on the observation of barium sulfate particle preparation and the aforementioned reasons, controllable synthesis of particles can be realized in the TC reactor. Therefore, as an extension, TC reactor was also applied to the other reactive synthesis system, the preparation of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ (NCM622) particles, using both CFD simulation and experimental validation. There are two main reasons for the choice of such particles. Firstly, lithium ion batteries have attracted many attentions in recent years due to their wide applications to electronic equipment and hybrid electronic vehicles. As one of the most promising cathode precursor materials, NCM622 has the potential to be commercialized. As the TC reactor used in this work can be scaled up into industrial application, the product properties can be easily compared with the commercially used materials. Secondly, after a careful review of previous studies, it is found that these studies mainly focused the optimization of chemical factors, but failed to realize the controllable particle synthesis to obtain regular shape. However, spherical particles are preferred among various morphologies. They often have high tap density, which is beneficial for the improvement of electrochemical performance. As confirmed in previous chapters, the turbulent eddied generated in the TC reactor are beneficial for the formation of compact agglomerates and regular spherical shape. Therefore, considering the above factors, NCM622 was chosen as a target object and the TC reactor is suitable for such reactive system. The experimental coprecipitation in the CTC and LTC focused on the effects of processing time and local turbulent shear rate. CFD simulation was employed to reveal the difference of flow field at various operating conditions. Both CFD simulation and experimental results show that the increased shear rate can lead to the decrease of the final synthesised micro-particle size due to the suppression of particle growth by turbulence eddy induced shear. Taylor-Couette flow by using the lobed inner cylinder can achieve an enhanced shear rate in the impinging jet regions formed in the vicinity of the inner cylinder surface due to the occurrence of a large radial velocity gradient. Consequently, the synthesised micro-particle properties such as morphology and specific surface area in the LTC are much more improved than those in the CTC. The mixing was also assessed and characterised by two variables, mean mixture fraction and its variance, predicted by use of CFD modelling with user-defined scalar (UDS), and correlating with the effect of shear rate for both the CTC and LTC. CFD simulation reveals that effective mixing at both the macro-scale and micro-scale can be quickly achieved in the LTC.

6.1 Introduction

Lithium ion batteries have commonly been recognised and widely employed as the most effective electric energy storage source and has received significant attention from various applications (Ren *et al.*, 2017). In order to manufacture the lithium ion batteries, the most commonly used transition metal elements for cathode materials are nickel, cobalt and manganese. However, LiNiO₂ is difficult to synthesise and has a poor thermal stability (Morales *et al.*, 1990). It has also been found that layered LiMnO₂ can easily be transformed into a spinel structure during charging and discharging processes. The spinel structure has a major drawback of the capacity fading due to the lattice distortion of manganese (Ceder and Mishra, 1999). On the other hand, many previous studies have indicated that LiCoO₂ can offer many advantages, such as high rate capability and excellent cycling performance, but its toxicity and high cost confines its application in industrial production (Liang *et al.*, 2014). Thus, some previous studies have focused on developing new cathode materials for lithium ion batteries, such as the partial replacement of single transition metal, or the development of new modification approaches, such as coating and doping (Kweon *et al.*, 2000; Kim *et al.*, 2006; and He *et al.*, 2012).

The layer ternary material LiNi_xCo_yMn_(1-x-y)O₂ series combines the advantages of LiNiO₂, LiCoO₂ and LiMnO₂, and demonstrates relatively high capacity, thermal stability and good cycling performance (Liang et al., 2014). Among this series of materials, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ has been commercially used. However, its low capacity (150-160 mAh/g) requires improvement (Lee et al., 2004). Nirich cathode materials are promising candidates due to their relatively high capacity and low cost, which can reach a capacity of up to 220 mAh/g with an average value of 170 mAh/g (Liang et al., 2014; and Yang et al., 2016). Among these Ni-rich cathode materials, LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (LiNCM622) has shown its considerable capacity at a low cut-off voltage range (< 4.3 V) and low cost with a rather low content of cobalt (Yuan et al., 2017). Cao et al. (2005) have obtained LiNCM622 with an initial discharge capacity of 175.3 mAh/g, which still manages to retain the capacity of more than 150 mAh/g even after 70 cycles. Sun et al. (2016) synthesised LiNCM622 at a high calcination temperature, and the material has shown a good low-temperature property (157 mAh/g at 0 $^{\circ}$ C). Chen et al. (2018) have successfully prepared concentration-gradient LiNCM622 via the co-precipitation method. The cathode material that they have synthesised has shown an excellent initial discharge capacity of up to 195.6 mAh/g with a capacity retention of about 90% after 100 cycles. All these studies have clearly demonstrated the importance of the synthesis process.

In order to obtain the final LiNCM622 cathode material, the first step is to synthesise the hydroxide precursor of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ (NCM622), followed by calcination with LiOH or Li₂CO₃. It has been suggested that LiNCM622 can inherit the morphology and structure from NCM622 precursor (Liang et al., 2014; Cheng et al., 2017; and Yuan et al., 2017), which means that the property of the final cathode material is dependent on the formation of the NCM622 precursor. Therefore, it is necessary to investigate the key operation parameters that are adopted in the reactors during the synthesis process of NCM622 precursor. Various synthesis methods have also been trialled and employed, such as spray-drying (Yue et al., 2011), solid-state method (Gan et al., 2005), sol-gel method (Lee et al., 2016). Most of these methods are intermittent with low productive efficiency, which is not beneficial to commercial and industrial applications. Compared to the aforementioned methods, co-precipitation is more efficient as it can be operated continuously, which is much more beneficial to large-scale production in industry. Also, the use of co-precipitation can achieve a relatively homogenous distribution of these three metals (Lee et al., 2004). Although a large amount of research work has been done, previous work has mainly focused on the impacts of factors such as the pH value of the solution, ammonia concentration and reactive environmental temperature (Cao et al., 2005; Liang et al., 2014; and Ren et al., 2017). Furthermore, the majority of the synthesis processes were conducted in the traditional stirring tank, resulting in a long processing time of at least 60 hours (Cui et al., 2019) and irregular shapes of NCM622 micro-particles.

Recent studies on the synthesis of micro-particles by precipitation have indicated that the hydrodynamics in the precipitation has a significant impact on the final particle size and morphology. Ren *et al.* (2017) used a stirred tank with the impeller of double blades to prepare the NCM622 precursor, and they obtained spherical secondary particles, formed from closely packed primary particles at 1000 rpm. In Liang et al.'s (2014) study, the effect of stirring speed was explored and it was observed that spherical particles exhibit a smooth surface and a high tap-density of 1.91 g/cm³ at 800 rpm. These studies have implicitly indicated that the synthesis of particles is very likely correlated with the local hydrodynamics involved, especially the local turbulence status. It should be also noted that these studies were only concerned with one hydrodynamic parameter, the stirring rate. Although the use of stirring speed can approximately expose the macro hydrodynamic environment for the formation of the particle suspension, it is still not able to reveal the relationship between the formation of the particles and the local hydrodynamics, which is suggested to be characterized by the local turbulence behaviour or turbulent shear. Zhu et al. (2019) have studied the utilisation of four different types of impeller to synthesise the NCM622 precursor. As a result, they suggested that the impeller may determine the hydrodynamics experienced by particle formation, affecting nuclei formation and the growth of primary particles. Their explanation on the mechanism involved in the synthesis lacks the support of theoretical analysis or CFD simulation of the flow taking place in the stirred tank. In addition, they have adopted a long processing time of at least 50 hours in their experiments in order to obtain regular spherical particles when using the traditional stirred tank reactor. The correlation between the processing time and the synthesised particle properties was not revealed.

The use of other types of reactor to prepare micro-fine particles was also reported in the literature. Typical examples are the T-mixer (Gradl *et al.*, 2006), impinging jet reactor (Casanova and Higuita, 2011), vortex mixer (Bensaid *et* al., 2014) and TC reactor (Thai et al., 2015). The common feature of these reactors is the enhancement and intensification of the local turbulence for the purpose of increasing the local turbulence induced shear. Among all these reactors, the TC reactor can be regarded as a promising device as it can provide controllable flow patterns and a narrow shear rate distribution (Li et al., 2015). To the best of our knowledge, only a few studies have reported the adoption of the TC reactor to synthesise the NCM622 precursor, but with the traditional rotational circular inner cylinder. The effect of the micromixing in such a reactor on the synthesised NCM622 particle properties is still not clear and requires further investigation. As numerous previous studies have investigated the effects of reactive parameters including pH value, ammonia concentration and reactive environmental temperature on particle synthesis process (Cao et al., 2005; Liang et al., 2014; and Ren et al., 2017), this study particularly focuses on the hydrodynamics in the synthesis of particles using the TC reactors, highlighting the effect of local turbulent shear rate on the formation and growth of particles. Also, the modelling of reactant mixing in the TC reactor but with two different inner cylinders, traditional circular inner cylinder and lobed inner cylinder is concerned. We aim to reveal how the use of different inner cylinders with cross-section profiles affect the mixing, including the correlation between the local turbulent induced shear and local micromixing. As turbulent flow in such a reactor is still not easily obtained from experimental measurement such as the use of PIV and LDV, a CFD modelling approach has been adopted in this study, coupling the mixing evaluation as suggested by Marchisio et al. (2006).

This chapter will be organised as follows. Section 6.2 will present the experimental details for co-precipitation of NCM622 precursor particles and characterisation while Section 6.3 will present the CFD modelling on the

synthesis in the TC reactor with micromixing mathematical modelling. Section 6.4 will present the numerical simulation results and discussion, focusing on the formation of synthesised particles and the correlation between the micromixing, and local turbulent shear. Section 6.5 will summarise the conclusions derived from the study.

6.2 Experimental

6.2.1 Apparatus setup

The apparatus of the TC reactor for the synthesis of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ (NCM622) precursor particles is schematically shown in Figure 6.1 (a). This particular setup consists of two cylinders with the inner cylinder rotating and the outer cylinder being static in the working mode. In order to reduce the effect of hydrostatic pressure, the reactor was placed horizontally, where the inlets and outlet were installed at the same level along the axial direction. Also, it was observed from the preparation of BaSO₄ particles in previous chapters that some gas bubbles may appear when feeding reactant solutions. Due to the buoyancy force, these bubbles will go throughout the whole reactor, leading to a perturbation, and unstable product properties. Additionally, under the effect of fluid gravity, Taylor vortex will be extruded, thus losing its original shape at the bottom of the reactor. The longer the reactor length, the more significant the shape changes. Thus, for a more precisely operation, TC reactor was located horizontally in NCM622 synthesis. Two types of inner cylinder that were adopted in the present study. One is the classical inner cylinder with a circular cross-sectional profile while the other is a lobed inner cylinder as shown in Figure 6.1 (b). Herewith, we use the abbreviations of CTC and LTC to denote the classical TC reactor and the lobed TC reactor, respectively. The dimensions of both types of reactor are described in Table 6.1.



Figure 6.1 (a) Schematic diagram of experimental apparatus; and (b) Schematic of cross-section profiles for the: (i) CTC; and (ii) LTC.

 Table 6.1 Dimensions of the TC reactor.

Dimension	CTC	LTC
Reactor length, L (mm)	160.00	160.00
Outer cylinder radius, r_o (mm)	60.00	60.00
Inner cylinder radius, r_i (mm)	54.00	53.80
Gap size, d (mm)	6.00	6.20

6.2.2 Co-precipitation synthesis of NCM622

The agents, nickel sulfate hexa-hydrate (NiSO₄·6H₂O, analytical grade), cobalt sulfate hepta-hydrate (CoSO₄·7H₂O, analytical grade) and manganese sulfate monohydrate (MnSO₄·H₂O, analytical grade) were chosen for the preparation of reactant solution. The molar ratio of the three mental ions (Ni:Co:Mn) was kept at 0.6:0.2:0.2 to form 2.0 mol/L sulfate (MSO₄) solution. A 4.0 mol/L sodium hydroxide (NaOH, analytical grade) solution was used as the precipitator. Ammonia (NH₃·H₂O, analytical grade) was supplied as the complexing agent, and the molar ratio of NH₃·H₂O to MSO₄ was kept at 1.0. In the present work, all gaents were purchased from Sinopharm Chemical Reagent Co., Ltd.

As pH is a critical factor in determining final product quality, a trial has been conducted preliminarily in identifying the appropriate pH value. Figure 6.2 (a) shows the colour change of upper liquid at the pH value of 11.3, 11.6, and 11.9. For a low pH value, the upper liquid is blue, which indicates too much ammonia complexation of metal ions formed rather than the metal hydroxide (Liang *et al.*, 2014). While, too high pH value will facilitate the formation of manganese oxide rather than manganese hydroxide, which makes the upper liquid brown (Lee *et al.*, 2004; and Liang *et al.*, 2014). Also, the SEM images in Figure 6.2

(b) indicates that at too low or too high pH value is not beneficial to form an irregular spherical NCM622 particles. At the pH value of 11.3, particles shows various morphologies with non-uniform size due to the random agglomeration of secondary particles. When pH value reaches 11.9, primary particles are assembled very loosely to form secondary particles without smooth surface.





Figure 6.2 (a) Product suspension colour; and (b) Product morphology at different pH values: (i) 11.3; (b) 11.6; and (c) 11.9.

The TC reactor was firstly filled with deionized water to remove air. The reactor was then heated to 55 °C and maintained at this particular temperature by using a heating jacket. A little amount of $NH_3 \cdot H_2O$ was pumped into the reactor at the base, followed by the synchronous feeding of MSO₄ solution and NaOH solution from individual inlets. Based on the volume of TC reactor, the total feeding rate contributed from the three inlets were adjusted to fix a mean

residence time of 1 hour, where the feeding rates of MSO₄ solution and NaOH solution were equal, and the feeding rate of ammonia was 1/3 of each reactant feeding rate. Meanwhile, during the co-precipitation process, the feeding rate of NaOH solution was adjusted slightly to maintain the pH value at 11.6 ± 0.05 . As NH₃·H₂O serves as complex agent to provide NH₃, firstly combining metal ions, the mechanism of the formation of NCM622 crystals can be expressed by two-step process.

$$\begin{aligned} 0.6Ni^{2+} + 0.2Co^{2+} + 0.2Mn^{2+} + nNH_3 \cdot H_2O \\ & \rightarrow [Ni_{0.6}Co_{0.2}Mn_{0.2}(NH_3)_n]^{2+} + nH_2O \\ [Ni_{0.6}Co_{0.2}Mn_{0.2}(NH_3)_n]^{2+} + 2OH^- + nH_2O \\ & \rightarrow Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2 + nNH_3 \cdot H_2O \end{aligned}$$

This co-precipitation was operated in a continuous mode, which ensures the reactants were continuously fed from inlets, and the synthesised micro-particle suspensions were continuously collected from the outlet. The key parameters are the processing time and the rotational speed of the inner cylinder in the CTC and LTC. After a given time period, the collected samples were washed with deionized water until the rinsed water was found to be neutral. Following this step, the suspension samples were then filtered and the filter cakes were dried at 80 °C for 24 h in the oven to obtain NCM622 precursor particles.

6.2.3 Characterisation

Particle size distribution of the synthesised NCM622 particles were determined by Malvern Mastersizer (Bettersize 2000, China). The corresponding morphology was observed using SEM (Sigma VP, ZEISS, Germany), coupled
with the confirmation of elemental composition by using energy dispersive Xray spectroscopy (EDX). The mass ratio of the three metal elements was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, SPECTRO ARCOS, Germany). Pore size and the specific area were measured using BET (Micromeritics ASAP 2020, U.S.A). The crystallite structure was analysed using XRD with Cu-K α radiation source (λ =1.54056 Å) (Bruker-AXS D8 advance powder diffractometer, Germany).

6.3 CFD modelling

6.3.1 Governing equations

The use of Reynolds number to describe the flow pattern in TC reactor has been suggested by many previous studies (Lathrop *et al.*, 1992; and Grossmann *et al.*, 2016), which is defined by

$$Re = \frac{\omega_i r_i d}{\nu} \tag{6.1}$$

where ω_i and r_i are the angular velocity and the radius of the inner cylinder, respectively, *d* is the gap size, and *v* is the kinematic viscosity. The critical Reynolds number (*Re_c*) serves as an indicator of the appearance of Taylor vortex flow. With the increase of angular velocity, the flow will undergo a series of instabilities until it develops into turbulent Taylor flow (Lathtop *et al.*, 1992). For the current study, the minimum rotational speed was set at 300 rpm, corresponding to a Reynolds number of 3728, which is far greater than the critical Reynolds number, *Re_c*=1728. Therefore, the flow in the reactor can be judged as turbulent flow. The turbulent flow field in the TC reactor was simulated with the Reynolds Average Navier-Stokes equations (RANS) coupled with RNG k- ε model to close the equations. The governing equations for continuity and momentum, and the RNG k- ε model are given as follows,

Continuity equation:

$$\nabla \cdot \boldsymbol{u} = 0 \tag{6.2}$$

Momentum conservation equation:

$$\frac{\partial}{\partial t}(\rho \boldsymbol{u}) + \nabla \cdot (\rho \boldsymbol{u} \boldsymbol{u}) = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \boldsymbol{g}$$
(6.3)

k equation:

$$\frac{\partial}{\partial t}(\rho k) + \nabla \cdot (\rho k \boldsymbol{u}) = \nabla \cdot \left(\frac{\mu_{eff}}{\sigma_k} \nabla k\right) + G_k - \rho \varepsilon$$
(6.4)

 ε equation:

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \nabla \cdot (\rho\varepsilon \boldsymbol{u}) = \nabla \cdot \left(\frac{\mu_{eff}}{\sigma_{\varepsilon}}\nabla\varepsilon\right) + C_{1\varepsilon}\frac{\varepsilon}{k}G_{k} - C_{2\varepsilon}\rho\frac{\varepsilon^{2}}{k} - R_{\varepsilon}$$
(6.5)

where u is the Reynolds-average velocity, ρ is the fluid density, p is the static pressure, τ is the stress tensor, g is the gravity. For k and ε equations, k is the turbulent kinetic energy, ε is the turbulent energy dissipation rate, μ_{eff} is the effective viscosity, σ_k and σ_{ε} are turbulent Prandtl numbers, G_k is the generation of turbulent kinetic energy, $C_{1\varepsilon}$ and $C_{2\varepsilon}$ are model constants, and R_{ε} is the extra

strain rate (Yakhot *et al.*, 1992). The details of flow field simulation refer to our previous study (Liu *et al.*, 2020).

6.3.2 Mixing model for co-precipitation synthesis

The mixing performance in the TC reactor that brings two separate flow streams of reactant (MSO₄ solution complexed with ammonia; NaOH solution) into contact to obtain NCM622 suspension particles can be evaluated by using the micromixing model, proposed by Fox (2003). The mixing efficiency can be described by a non-reacting scalar, mixture fraction ξ . For a non-premixed reaction system, (A+B \rightarrow P), the mixture fraction is a conserved scalar, which is related to the local concentration of reactants A and B, defined by

$$\xi = \frac{c_A - c_B + c_{B_0}}{c_{A_0} + c_{B_0}} \tag{6.6}$$

where c_{A_0} and c_A are the initial concentration and the local concentration of reactant A, c_{B_0} and c_B are the initial concentration and the local concentration of reactant B. By definition, the value of mixture fraction will fall into the range between 0 and 1, indicating the degree of local mixing under the influence of turbulent shear flow condition for CFD modelling. The Reynolds-average transport equation to describe such scalar can be written as (Fox, 2003),

$$\frac{\partial \rho \bar{\xi}}{\partial t} + \nabla \cdot (\rho \boldsymbol{u} \bar{\xi}) = \nabla \cdot (\rho \Gamma_T \nabla \bar{\xi})$$
(6.7)

where Γ_T is the turbulent diffusivity. It can be calculated using the turbulent Schmidt number and Boussinesq hypothesis by the following equation,

$$\Gamma_T = \frac{C_\mu}{Sc_t} \frac{k^2}{\varepsilon} \tag{6.8}$$

where C_{μ} is a constant equal to 0.09, and the turbulent Schmidt number Sc_t takes a value of 0.7. However, the mean mixture fraction is unable to describe the actual turbulent scalar fluctuations. This information is suggested to be provided by another variable, mixture fraction variance $\overline{\xi'}^2$ (Liu and Fox, 2006; Marchisio *et al.*, 2006; and Duan *et al.*, 2016). Theoretically, for a perfect mixing region, the value of $\overline{\xi'}^2$ should be zero due to no segregation existence. The Reynolds-average transport equation for $\overline{\xi'}^2$ is given as follows,

$$\frac{\partial \rho \overline{\xi'^2}}{\partial t} + \nabla \cdot (\rho \boldsymbol{u} \overline{\xi'^2}) = \nabla \cdot (\rho \Gamma_T \nabla \overline{\xi'^2}) + 2\rho \Gamma_T |\nabla \overline{\xi}|^2 - 2\rho \gamma \overline{\xi'^2}$$
(6.9)

The second term on the right hand is the production term, which is generated by the gradients of the mean mixture fraction. The last term is the dissipation term due to micromixing. In order to solve the equation, a closure for this term is necessary. The micromixing parameter γ is modelled using the following approximation (Fox, 2003),

$$\gamma = \frac{C_{\Phi}}{2} \frac{\varepsilon}{k} \tag{6.10}$$

where γ is defined as the micromixing rate. C_{ϕ} denotes the mechanical-totimescale ratio (Bensaid *et al.*, 2014) and is a function of local Reynolds number of the turbulent eddies with the Schmidt number larger than 1000. For a fully turbulent flow, C_{ϕ} is found to be around 2.0. In addition, the characteristic decay time t_{ϕ} for sub-scale segregation can be estimated according to Equation (6.11),

$$t_{\Phi} = \frac{1}{2\gamma} \tag{6.11}$$

where t_{Φ} can be further interpreted as the local micromixing time, which is the time required to destroy micro-scale gradient within sub-grid scale to achieve complete mixing at molecular level.

6.3.3 Numerical modelling

CFD modelling of the turbulent vortex flow in the TC reactor was conducted using commercial software, Fluent 17.0. The computation domain was set up with the Design Modeller while the computational mesh was created using ANSYS ICEM. For modelling of the flow in the LTC, a sliding mesh was adopted in the vicinity of the inner cylinder due to the lobed cross-section profile. The gap region between the inner cylinder and the outer cylinder was divided into two zones, where the inner one contained the lobed inner cylinder, whose rotational speed was set by mesh motion. The total meshes of the computational domain have around 400000 cells. As the mesh size in the radial direction is crucial for identification of the detailed structure of Taylor vortices and the local velocity gradient, the trial simulation on mesh independence check was conducted by only changing the node number along the radial direction with the meshes of 10×180×160, 14×180×160. and 24×180×160 (radial×circumferential×axial). The trial simulation results have shown that the differences between the two setups of 14×180×160 and 24×180×160 are marginal, indicating that the former mesh adopted has been fine enough to ensure numerical accuracy. The mesh $14 \times 180 \times 160$ has thus been adopted in the numerical modelling of the turbulent flow and micromixing in the TC reactor.

The boundary conditions at inlets and outlet were set as velocity inlet and pressure outlet, respectively. The convergence criteria for the simulation was set at 1.0×10^{-3} , and the time step size was set at 10^{-4} s for temporal discretisation. The QUICK scheme has been applied for the spatial discretisation of the convective terms, and the pressure-velocity coupling was realised by the SIMPLEC algorithm.

The micromixing model was implemented by the user defined scalar (UDS) into FLUENT to predict the mixing performance of the reactants, where the mean mixture fraction $\overline{\xi}$ and the mixture fraction variance $\overline{\xi'}^2$ were solved using Equations (6.7) and (6.9) with $X_1 = \overline{\xi}$, and $X_2 = \overline{\xi'}^2$. The initial boundary conditions at the inlet for the MSO₄ solution were $X_1 = 1.0$, and $X_2 = 0.0$, and for NaOH solution were $X_1 = 0.0$, and $X_2 = 0.0$. Since the solution density and viscosity are constant, the flow field in the reactor can be calculated firstly, independent of other scalars' transport equations. The scalars of micromixing model were solved with the first order upwind scheme after the turbulent vortex flow field was obtained. The convergence criteria of both scalars were set at 1×10^{-4} .

6.4 Results and discussion

6.4.1 Effects of processing time and the local turbulence induced eddies in the TC reactor on the synthesised particle properties

The co-precipitation reaction was driven by local supersaturation, generated from the contact of the feeding solutions. Generally, for a continuous feeding mode, a time period is necessary for the products to reach a steady state. In the current study, the processing time is defined as the time elapsed from the reaction startup to the end of sample collection. In order to determine such a time period, the collection of the synthesised NCM622 particles were continuously trialled from the reactor outlet for a specified time interval, which is equal to the mean residence time (i.e., 1 h). The processing time ranges from 1 hour to 8 hours.

Figure 6.3 (a) shows the evaluation of particle morphology with processing time at a mean shear rate of 1604 s⁻¹, calculated by using Equation (6.16) and corresponds to an inner cylinder of rotational speed at 1100 rpm, and the Reynolds number of 13668 in the CTC. From the SEM images, it can be seen clearly that the final NCM622 particles are the secondary particles, assembled by the very thin sheet-like primary particles. These secondary particles were formed as the result of agglomeration. At the onset of the reaction, the initial form of primary particle is crystallite.

In addition, the composition of the synthesised particles were identified by EDX. Figure 6.3 (c) shows the elemental distribution of Ni, Co and Mn respectively at a processing time of 8 hours. The individual images and the merged image indicate a homogenous distribution of these three metals. In order to further ensure the components are properly presented in final NCM622 particles, the mass ratio of nickel, cobalt and manganese were measured and then converted into molar ratio, shown in Table 6.2. It can be seen that there is no significant difference in terms of molar concentration of three major elements between the processing time at 7 hours and 8 hours. Also, the molar ratio is near to the prescribed ratio of 0.6:0.2:0.2. This result indicates that the proper NCM622 precursor particles can be synthesized within a short processing time by using the TC reactor. Thus, the TC reactor is suggested to be a promising device to increase productivity.





(b)





Figure 6.3 (a) SEM images of NCM622 in the CTC; and (b) LTC at different processing times: (i) 1 h; (ii) 2 h; (iii) 3 h; (iv) 4 h; (v) 5 h; (vi) 6 h; (vii) 7 h; and (viii) 8 h; and (c) elemental mapping at a processing time of 8 hours.

Р	Processing time (hours)	Mass ratio wt%			Molar ratio						
		Ni	Со	Mn	Ni	Со	Mn				
	7	39.4	14.1	12.6	0.59	0.21	0.20				

13.9

8

39.8

 Table 6.2 Element concentration.

The XRD pattern in Figure 6.4 shows the crystal structure of NCM622, which is similar to the crystal structure of β -Ni(OH)₂. All diffraction peaks present a typical hexagonal structure with a space group of $P\overline{3}m1$. The result indicates that Mn²⁺ and Co²⁺ entered the internal lattice structure of Ni(OH)₂, substituting

12.4

0.59

0.21

0.20

some Ni²⁺ (Lee *et al.*, 2004; Thai *et al.*, 2015; and Xu *et al.*, 2018). This is the reason for the absence of the diffraction peaks of Mn(OH)₂ and Co(OH)₂ as shown in Figure 6.4. The high intensity of plane (001), plane (100), and plane (101) reveals the orientation of crystal growth (Thai et al., 2015). Moreover, the relatively broader full width at the half maximum height (FWHM) of plane (001) indicates a smaller crystallite size, calculated using the Scherrer equation, given by Equation (6.15). Furthermore, it can be deduced from the different sizes of the three typical planes that planes (001) and (101) are thinner, while plane (100) is longer, which indicates a plate-like primary particles synthesised initially. It can be postulated that due to highly intensive turbulent eddy fluctuation, the existing primary particles trapped by small eddies may collide with each other. This collision can lead to the formation of the loosely packed aggregates (marked in Figure 6.3 (a)), which will be transported and re-dispersed under the influence of various size turbulent eddies. Figure 6.5 illustrates the radial velocity field in the vertical cutting plane. It can be seen that Taylor vortices are present in terms of a pair of counter-rotating toroidal vortices, highlighted in Figure 6.5. There exists either radially inward or outward impinging jet regions between Taylor vortex pairs. The local large velocity gradient generated in the impinging jet regions results in the high shear rate. Such strong local turbulent shear generates the turbulent eddies that trap the crystallites and cause the collision among the crystallites, thus affecting the aggregation of the nuclei particles. This dynamic process can be interpreted by using the Stokes number, defined by

$$St_{\eta} = \frac{\tau_p}{\tau_f} \tag{6.12}$$

where τ_p is the particle dynamic response time, and τ_f can be interpreted as the characteristic time of the locally generated turbulent eddies. τ_p and τ_f can be estimated by the following Equation (6.13)

$$\tau_p = \frac{\rho_p d_p^2}{18\mu}; \quad \tau_f = \sqrt{\frac{\nu}{\varepsilon}} \tag{6.13}$$

$$St_{\eta} = \frac{\rho_p}{18\mu\rho_L} \left(\frac{d_p}{\eta}\right)^2 \tag{6.14}$$

where ρ_p and ρ_L are the particle density and the solution density, respectively, and d_p is the particle size. η is the Kolmogorov turbulent eddy scale. Normally, if $St_\eta < 1$, it indicates that particles will be trapped by the turbulent eddies, thus increasing the possibility of particle aggregation due to the collision so as to promote the growth of particle size, but will be also be confined by the eddy induced shear. It should be noted here that $\sqrt{\frac{\nu}{\varepsilon}}$ is the typical turn-over time of the locally generated turbulent eddies due to the turbulence induced shear.



Figure 6.4 XRD results of crystallite at different shear rates in the: (a) CTC; and (b) LTC.



Figure 6.5 Radial velocity distribution in the vertical cutting plane of the CTC.

In order to calculate particle Stokes number of individual crystallites, the average crystallite size should be obtained first, which is estimated by the Scherrer equation

$$D = \frac{\kappa\lambda}{\delta cos\theta} \tag{6.15}$$

where *K* is the shape factor, equal to 0.89 for NCM622 particles, λ is the wavelength of X-ray radiation, equal to 0.145056 nm, δ is the peak width at half minimum height, and θ is the diffraction angle. The crystallite size was calculated at different processing time from 1 to 8 hours, and the value ranges from 12 nm to 23.6 nm. Thus, there is little difference in crystallite size, which indicates that a single crystallite is hardly changed with processing time. Furthermore, the crystallite Stokes number was calculated with the order of 10⁻

⁷, which is much smaller than 1.0. This indicates that primary particles are closely transported and trapped by turbulent eddies. SEM images indicates that at the initial several hours, primary particles were loosely packed, forming aggregates. With an extension of the processing time, a long-term effect of entrapment leads to the agglomeration among these aggregates. Aggregates are stacked closely and bonded strongly. It has been observed from Figure 6.3 that the secondary particles at the processing time of 8 hours get more compact. Additionally, due to the long-time exposure to the local turbulent eddy induced shear, the surface of secondary particles becomes smooth, and the shape looks regular and spherical-like.

We also tested particle size and its distribution, as shown in Figures 6.6 (a) and 6.6 (b). The average particle size is small initially and increases until reaching a maximum, followed by a decreasing average size until levelling off. This trend is consistent with the formation mechanism of secondary particles. As the irregular and loosely packed aggregates are formed at first, there is not much reactant accumulating locally. However, with more reactants engulfed and trapped in eddies, the micro gaps among the aggregates are fully filled, and the local turbulent shear acting on the surfaces of these aggregates to shear off those of micro irregularity so as to yield regular shapes. It has been suggested by Ying et al. (2001) and Ying et al. (2004) that among various morphologies, the spherical one is the most effective in terms of packing density, as it has a rather small contact interface, which can lead to the least potential for bridge formation between particles. While the tap density of LiNCM622 cathode materials are generally dependent on the tap density of NCM622 precursors, it can be hypothesised that a high tap density may be beneficial for high electrical performance in terms of long life cycling (Liang et al., 2014). Figure 6.6 (b) illustrates the particle size distribution obtained at different processing times. The uniform distribution from the start of the particle formation suggests that the advantage of using the TC reactor for co-precipitation of micro particles is that it can provide relatively uniform turbulent shear distribution in the reaction chamber.



Figure 6.6 (a) Particle size of NCM622 at different processing times in the CTC; and (b) Particle size distribution.

Some of the previous studies have indicated that the final NCM622 particles are secondary particles, assembled by a large number of nano-scaled primary particles (Thai *et al.*, 2015; Mayra and Kim, 2015; and Zhu *et al.*, 2019). By carefully observing the results of particle morphology and size from Figures 6.3 (a) and 6.6, it is suggested that the particles with a regular shape and a critical size can be obtained after the processing time exceeds 7 hours. Therefore, for the co-precipitation system of NCM622 precursor synthesis using the TC reactor in this study, the co-precipitation deems to reach the steady state after 7 hours, which is much shorter than that of using the traditional mixing tank reactor or continuous stirred tank reactor (CSTR). Considering this, the

experimental validation and analysis have taken the processing time to be 8 hours.

6.4.2 Effect of the cross-section profiles of inner cylinder and the mean shear rate

As the type of the rotational inner cylinder affects the Taylor vortices formed and the local turbulent shear flow behaviour, a lobed inner cylinder was also employed in the present study for assessing the effect of the cross-section profiles of inner cylinder on particles. The cross-sectional profile of this lobed geometry is composed of three arcs with the identical radian of 120°, connected by three mutual tangential lines. Investigations of the two geometries were conducted at different mean shear rates by the adoption of different rotational speeds. We employ the mean shear rate to characterise the effect of the turbulence induced shear instead of the rotational speed, as the mean shear rate is the overall effort contributed from the inner cylinder rotation, the gap size (affecting the volume for co-precipitation) and the type of the inner cylinder. The average mean shear rate in the TC reactor can be calculated by the following equation (Serra *et al.*, 1997),

$$\bar{G} = \sqrt{\frac{\bar{\varepsilon}}{\nu}} \tag{6.16}$$

The average turbulent dissipation rate $\bar{\varepsilon}$ was obtained from CFD simulation.

Table 6.3 summarises the values of shear rate, and corresponding primary particle size. It can be seen that the size of primary particles has little difference,

ranging from 12 nm to 23.6 nm. We also estimated the Kolmogorov length scale by Equation (6.17).

$$\eta = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4} \tag{6.17}$$

Apparently, the Kolmogorov length scale has the order of 10^{-5} m, which is much larger than the size of primary particles. Therefore, turbulent eddy shear has a very weak effect on crystallisation. Primary particles were only trapped, and then entrained by eddies. The comparison of length scale can also be found in Kim *et al.*'s (2011) study. However, their study only pointed out that fluid shear can act on particle size, but failed to interpret the interaction mechanism between them with different orders of length scale.

Table 6.3 Summary of flow field parameters and primary particle size at different rotational speeds.

Rotational	Reynolds number <i>Re</i>		Shear rate $G(s^{-1})$		Kolmogorov length scale η		Primary particle size <i>D</i>	
speed $oldsymbol{arDelta}$								
(rpm)					(×10 ⁻⁵ m)		(nm)	
	CTC	LTC	CTC	LTC	CTC	LTC	CTC	LTC
300	3728	3837	126.9	483.5	14.67	7.51	14.5	15.1
500	6213	6396	550.9	897.5	7.04	5.52	23.6	19.9
700	8698	8954	1042.4	1373.4	5.12	4.46	14.5	13.7
1100	13668	14071	1603.9	2465.5	4.13	3.33	17.1	18.6
1500	18638	19188	2858.2	3690.7	3.09	2.72	12.0	16.4

The effects of the inner cylinder types and the corresponding shear rates on the crystal structure of the primary particles are illustrated in Figure 6.4. First of all, typical planes of (001), (100), (101), and (102) are shown in the XRD pattern. In addition, for the same inner cylinder cross-sectional profile, the appearance of characteristic diffraction peaks is almost not affected by adopting different mean shear rates for both the CTC and LTC. However, it is found that the peak intensity of planes (100) and (101) for the LTC increases with the increase of the mean shear rate greater than that for the CTC, indicating an improved crystallinity of primary particles. Such a growth preference were also observed in the works of Kim et al. (2011); Yang et al. (2016) and Wei et al. (2010). Crystal growth along plane (100) will show a good electrochemical performance, as plane (100) can provide proper paths for the fast transportation of lithium ion as suggested in these studies. Moreover, the relative peak intensity of plane (001) to plane (101) is different for the CTC and LTC. In the CTC, the crystal growth is mainly along plane (001), while in the LTC, the growth of plane (101) is faster than plane (001). This result also indicates the orientation of crystal growth under the influence of the local turbulent shear field.

The comparison of secondary particles in terms of the tap density, morphology, size and porosity has also been carried out at different mean shear rates for the CTC and LTC. Figure 6.3 (b) shows the evaluation of particle morphology with processing time in the LTC at the same rotational speed as the CTC. It is obvious that at the initial several hours, particles fail to be assembled with a regular shape in both the reactors. However, after 5 hours, the synthesized particles in the LTC present advantages in terms of spherical morphology, uniform size, and compact agglomeration. Figure 6.7 shows the change of particle size with

the increase of mean shear rate. The experimental validation was conducted by changing the rotational speed of the inner cylinder. For the same rotational speed, the mean shear rate in the LTC is greater than that in the CTC. For the CTC, the average particle size continuously decreases to 4 µm. In contrast, for the LTC, the particle size increases at smaller mean shear rate but gradually decreases to 6 µm. Furthermore, particle size synthesised in the LTC is greater than that synthesised in the CTC for the whole range of mean shear rates. Changes of the Kolmogorov length scale are also shown in Figure 6.7, where the Kolmogorov scale is calculated based on Equation (6.17). It can be seen from Figure 6.7 that the estimated Kolmogorov length scale is slightly greater than the particle size but they have the same order of magnitude. It should be noted here that the difference between the secondary particle size and the estimated Kolmogorov length scale is smaller for the LTC than that for the CTC. This finding indicates that the secondary particles may not only be well entrained by the turbulent eddies, but are still exposed to the turbulent eddy induced shear. By carefully inspecting the SEM results shown in Figure 6.8, it can be observed that the shape of NCM622 particles is regular with a sphericallike and smoother surface when increasing the mean shear rate. This effect is consolidated when using the LTC. In addition, Figure 6.9 shows the increased tap density of the NCM622 particles with the increase of shear rate. For the LTC, a high tap density of 2.25 g/cm³ was reached at the shear rate of 3690.7 s⁻¹, which is larger than previously reported values (Thai et al., 2015; and Liang et al., 2014). Generally, the regular spherical particles can be compactly accumulated, which is beneficial for long life cycling (Liang et al., 2014).



Figure 6.7 Particle size and Kolmogorov length scale at different shear rates.



(a)



Figure 6.8 SEM images of NCM622 at different shear rates for the (a) CTC: (i) 126.9 s⁻¹; (ii) 550.9 s⁻¹; (iii) 1042.4 s⁻¹; (iv) 1603.9 s⁻¹; (v) 2858.2 s⁻¹; and (b) LTC: (i) 483.5 s⁻¹; (ii) 897.5 s⁻¹; (iii) 1373.4 s⁻¹; (iv) 2465.5 s⁻¹; (v) 3690.7 s⁻¹.



Figure 6.9 Tap density at different shear rates for the CTC and LTC.

The N_2 adsorption and desorption isotherm, and specific surface area of NCM622 particles are illustrated in Figures 6.10 (a), (b) and (c). The high porosity reflects more pores existing in the internal structure of particles. When

a large number of primary particles aggregate to form the secondary particle, pores will be generated in its internal while a loosely aggregated and packed structure leads to a high porosity. At smaller shear rates, aggregates fail to be combined compactly. Consequently, high porosity results from the loosely assembled aggregates. With increasing the shear rate, more primary particles entrapped by eddies can fill up the gaps among aggregates, developing into a rather regular shape. This result can be evidenced by examining the SEM images from the local amplification of those secondary particles as shown in Figure 6.10. It is obvious that with the increase of shear rate, particles are assembled compactly from the structure out-appearance, especially in the case of the LTC.



Figure 6.10 N₂ adsorption/desorption isotherm at different shear rates in the: (a) CTC; and (b) LTC; (c) Specific surface area at different shear rates.

The above results and discussion have shown the existence of strong correlation between the synthesised particle properties and the turbulent eddy shear rate. It can be deduced that the local turbulent shear controls both primary and secondary particle growth and collision, assembly and agglomeration of aggregates. The turbulent eddy induced shear force can act on the surface of secondary particles as shown schematically in Figure 6.11. According to Sung *et al.*'s (2000) study, the size of yttrium oxalate agglomerates increases with the increase of agitation speed until 700 rpm, suggesting that if turbulent shear is not enough to overcome the interactive force between agglomerates, particles will keep continuous growth. In Thai *et al.*'s (2015) study, they found that when the rotational speed of TC crystallizer exceeds 300 rpm, shear force will be stronger than interactive force. Our study has shown that the synthesised particle properties are strongly affected by the turbulent eddy shear rate that correlates with the rotational speed and the cross-sectional profiles of inner cylinder of the TC reactor.



Figure 6.11 Schematic representation of particles in a turbulent shear flow.

Figure 6.12 shows the time averaged velocity field and shear strain rate in the CTC and LTC. Both cases take three rotational speeds, 500 rpm, 1100 rpm, and 1500 rpm, respectively, for comparisons. It can be seen from the figure that both the mean velocity and the shear strain rate in the impinging jet regions formed in the vicinity of the inner cylinder surface between the two Taylor vortices are strengthened with the increase of the mean shear rate. As the velocity gradient increases, the entrapment effect due to the local turbulent shear is enhanced. This effect becomes remarkable, especially for the LTC, as the lobed inner cylinder generates the periodic variation of gap size. Gap area is critical for the identification of flow pattern, and the impinging jet flows also occurs in such an area. Firstly, it can be seen from Equation (6.1) that Reynolds number which is used to determine global turbulence degree, depends on the gap size. For the constant gap size in the CTC, turbulent condition can be hardly changed significantly once the rotational speed is given. However, for the LTC, the gap

size becomes temporal-periodic, which keeps changing with the rotation of the inner cylinder, and this variation may generate the local flow separation behind the top of lobed inner cylinder so as to induce more turbulent eddies locally. In this case, the formation and the deformation of Taylor vortex always exist, thus Taylor vortex with a constant size cannot be created, Accordingly, more turbulent eddies can be induced compared to the CTC. These eddies will further interact with particles. On one hand, eddy entrapment contributes to the compactness of agglomerates. On the other hand, small eddies down to the Kolmogorov scale are generally recognised to be isotropic. This indicates an evenly distributed eddy shear acting on particle surface, which will eventually result in the formation of particles with regular shape. Secondly, as can be seen from Figure 6.12 (a) that the jet velocity is enhanced in the large gap area when employing the LTC. Due to the relative high velocity of jet flows impinging to the wall, more turbulent eddies will be created, thus the local turbulent shear is enhanced. Therefore, the aforementioned factors in the gap area may contribute to the formation of desired particle properties in the LTC.



(a)



Figure 6.2 (a) Radial velocity distributions; and (b) Shear strain rate distribution at different inner cylinder rotational speeds: (i) 500 rpm; (ii) 1100 rpm; and (iii) 1500 rpm.

6.4.3 Micromixing

As can be seen from the previous discussion, hydrodynamic micromixing plays an important role in the co-precipitation process in the TC reactor, which has a significant impact on the synthesized particle properties. Generally speaking, fast mixing can result in the high local supersaturation, which will further facilitate nucleation process. The increase of nucleation rate is beneficial to the creation of a large number of primary particles, thus leading to a small particle size. To this end, particle size may be seen as an indicator of the degree of mixing at all the scales, including macro level to molecular level.

Figure 6.13 shows the values of the variations of the mean mixture fraction $\bar{\xi}$ with time in the middle cylindrical surface of the gap. By definition, $\bar{\xi}$ ranges from 0.0 to 1.0, and the value of 0.5 is deemed to achieve a perfect macromixing, thus giving out a homogenously completed mixing. In our CFD modelling, $\bar{\xi}$ was assumed to 0.0 at the inlet of MSO₄ solution, and 1.0 at the inlet of NaOH solution. It can be seen from the figure that the mixing condition

is poor inside the reactor at the onset of reactants injection. A value of ξ far from 0.5 often indicates a non-homogeneous environment. This could be the reason for the appearance of irregular particle morphology at the first several hours of the co-precipitation synthesis, observed from the SEM images. The value of ξ gradually approaches 0.5 with time, indicating an effective mixing to be achieved. It is interesting to note that the time to attain a relatively good mixing required for the LTC is shorter than that for the CTC. This clearly indicates a relatively fast formation of well-established macro-mixing condition in the LTC. Furthermore, high mean shear rate can also improve the mixing at macro scale. As can be seen from the figure, the time for setting-up of the macro mixing becomes shorter with the increase of the mean turbulent shear rate, but this difference disappears when the rotational speed of the inner cylinder is greater than 1100 rpm.



(a)



Figure 6.33 Mean mixture fraction $\overline{\xi}$ in the middle cylindrical surface of the gap for the: (a) CTC; and (b) LTC at different inner cylinder rotational speeds: (i) 500 rpm; (ii) 1100 rpm; and (iii) 1500 rpm.

Since the co-precipitation chemical reaction occurs at molecular level, the other variable for characterisation of the micromixing, the mixture fraction variance $\overline{\xi'}^2$ is used here to estimate the degree of micromixing. Figure 6.14 illustrates the distribution of the variance ratio $(\overline{\xi'}^2/\overline{\xi'}^2_{max})$ along the circumferential direction in the vertical cutting plane. Such distribution is used to characterise the micromixing performance due to geometrical modification. It can be seen that high values of $\overline{\xi'}^2$ mainly concentrate in the inlet regions, which decrease with the rotation of the inner cylinder. The mixing process can be described as follows. After reactants are introduced into the system, large-scale variance is generated, but smoothed out by the turbulent diffusion with small-scale variance to be dissipated by molecular diffusion. Turbulent eddy shear facilitates the mixing process, thus creating a uniform environment and small variance. To

effectively describe such micromixing behaviour, a correlation coefficient between $\overline{\xi'^2}$ and the cross-sectional average turbulent energy dissipation rate $\overline{\varepsilon}$ in the circumferential direction for the given axial position of the reactor is introduced as defined by

$$R = \frac{\overline{\xi'^2(\theta)} \cdot \overline{\varepsilon}(\theta)}{\sqrt{\overline{\xi'^2}^2(\theta)} \cdot \sqrt{\overline{\varepsilon}^2(\theta)}}$$
(6.18)

Figure 6.15 shows the results of correlation coefficient *R* in the circumferential direction around the inner cylinder. Such correlation may be used to forecast the position of good micromixing so that the cross-sectional profiles of inner cylinder can be altered accordingly. It is revealed from Figure 6.15 that more peaks of *R* are observed in the CTC than those in the LTC when using the same rotational speed. However, the non-zero value of $\overline{\xi'}$ often indicates poor micromixing. The large value of *R* suggests a greater local turbulent energy dissipation and poor micromixing environment. By comparing Figures 6.15 (a) and (b), it can be clearly observed that the number of peaks of *R* is reduced for the case of using the lobed inner cylinder, indicating that the micromixing occurring in the LTC is better than that in the CTC. This implies that the micromixing behaviour can be improved through the alteration of the cross-sectional profiles of inner cylinder for the TC reactor.



Figure 6.4 Distribution of the ratio of mixture fraction variance $(\overline{\xi'^2}/\overline{\xi'^2}_{max})$ for the: (a) CTC; and (b) LTC at different inner cylinder rotational speeds: (i) 500 rpm; (ii) 1100 rpm; and (iii) 1500 rpm.



Figure 6.5 Spatial correlation between mixture fraction variance and turbulent energy dissipation rate for the: (a) CTC; and (b) LTC.

6.5 Conclusions

Modelling of co-precipitation synthesis of NCM622 precursor for cathode material of lithium ion batteries in the TC reactor with classical circular and lobed inner cylinder profiles has been carried out by CFD simulation and experimental validations. The effects of processing time, inner cylinder type and the turbulent mean shear rate on the co-precipitation synthesis of micro-particles were investigated. The main conclusions reached from the present study are as follows:

(1) The employment of the TC reactor for synthesis of micro-particles can significantly reduce the processing time. In particular, the impinging jet region created in the middle of a pair of counter-rotating toroidal vortices increases the turbulent shear gradient, thus the shear rate.

(2) The local turbulent shear imposed to the synthesised suspension particles can either increase the size of particles or inhibit the growth of particles. For those particles whose size is much smaller than the Kolmogorov length scale, turbulent eddies can enhance the entrapped particle collision, thus resulting in more particles aggregation to form large size particles. However, once the shear force caused by the turbulent eddy exerting on agglomerates exceeds the internal bonding force among the agglomerates, the size of agglomerated particles will be suppressed. Also, the periodic variation of gap size for lobed inner cylinder in the LTC is beneficial to the generation of increased velocity gradient in the impinging jet regions, yielding a strong local turbulent energy dissipation rate.

(3) The mixing behaviour of reactants (MSO₄ solution and NaOH solution) was assessed using CFD modelling. It is revealed from the simulation that the mean

mixture fraction $\bar{\xi}$ representing the mixing degree at macro scale can take a shorter time to reach the required mixing condition for NCM622 coprecipitation synthesis at a higher shear rate, especially for the LTC. The micro scale mixing, characterised by the mixture fraction variance $\bar{\xi'}^2$, the key indicator to evaluate local supersaturation for molecular reaction, has a strong correlation with the turbulent energy dissipation rate. This correlation can be used for the evaluation of the micromixing performance, which may assist the selection of different cross-sectional profiles of the inner cylinder in the TC reactor for co-precipitation synthesis of micro-particles with better properties.

References

- Bensaid, S., Deorsola, F.A., Marchisio, D.L., Russo, N. and Fino, D., 2014. Flow field simulation and mixing efficiency assessment of the multi-inlet vortex mixer for molybdenum sulfide nanoparticle precipitation. *Chemical Engineering Journal*, 238, pp.66-77.
- Cao, H., Zhang, Y., Zhang, J. and Xia, B., 2005. Synthesis and electrochemical characteristics of layered LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material for lithium ion batteries. *Solid State Ionics*, *176*(13-14), pp.1207-1211.
- Casanova, H. and Higuita, L.P., 2011. Synthesis of calcium carbonate nanoparticles by reactive precipitation using a high pressure jet homogenizer. *Chemical Engineering Journal*, *175*, pp.569-578.
- Ceder, G. and Mishra, S.K., 1999. The Stability of Orthorhombic and Monoclinic-Layered LiMnO2. *Electrochemical and Solid State Letters*, 2(11), p.550.
- Chen, X., Jia, X., Qu, Y., Chen, D. and Chen, Y., 2018. High-voltage performance of concentration-gradient Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂ layered oxide cathode materials for lithium batteries. *New Journal of Chemistry*, 42(8), pp.5868-5874.
- Cheng, K.L., Mu, D.B., Wu, B.R., Wang, L., Jiang, Y. and Wang, R., 2017. Electrochemical performance of a nickel-rich LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material for lithium-ion batteries under different cut-off voltages. International Journal of Minerals, *Metallurgy*, and Materials, 24(3), pp.342-351.
- Cui, Y., Liu, K., Man, J., Cui, J., Zhang, H., Zhao, W. and Sun, J., 2019. Preparation of ultra-stable Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O₂ cathode material with a

continuous hydroxide co-precipitation method. *Journal of Alloys and Compounds*, 793, pp.77-85.

- Duan, X., Feng, X., Yang, C. and Mao, Z.S., 2016. Numerical simulation of micro-mixing in stirred reactors using the engulfment model coupled with CFD. *Chemical Engineering Science*, 140, pp.179-188.
- Fox, R.O., 2003. Computational Models for Turbulent Reacting Flows. Cambridge university press.
- Gan, C., Hu, X., Zhan, H. and Zhou, Y., 2005. Synthesis and characterization of $Li_{1.2}Ni_{0.6}Co_{0.2}Mn_{0.2}O_{2+\delta}$ as a cathode material for secondary lithium batteries. *Solid State Ionics*, 176(7-8), pp.687-692.
- Gradl, J., Schwarzer, H.C., Schwertfirm, F., Manhart, M. and Peukert, W., 2006.
 Precipitation of nanoparticles in a T-mixer: coupling the particle population dynamics with hydrodynamics through direct numerical simulation. *Chemical Engineering and Processing: Process Intensification*, 45(10), pp.908-916.
- Grossmann, S., Lohse, D. and Sun, C., 2016. High–reynolds number taylorcouette turbulence. *Annual Review of Fluid Mechanics*, *48*, pp.53-80.
- He, P., Yu, H. and Zhou, H., 2012. Layered lithium transition metal oxide cathodes towards high energy lithium-ion batteries. *Journal of Materials Chemistry*, 22(9), pp.3680-3695.
- Kim, M.H., Shin, H.S., Shin, D. and Sun, Y.K., 2006. Synthesis and electrochemical properties of Li [Ni_{0.8}Co_{0.1}Mn_{0.1}]O₂ and Li [Ni_{0.8}Co_{0.2}]O₂ via co-precipitation. *Journal of Power Sources*, 159(2), pp.1328-1333.
- Kim, J.M., Chang, S.M., Chang, J.H. and Kim, W.S., 2011. Agglomeration of nickel/cobalt/manganese hydroxide crystals in Couette–Taylor crystallizer. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 384(1-3), pp.31-39.

- Kweon, H.J., Kim, S.J. and Park, D.G., 2000. Modification of LixNi1– yCoyO2 by applying a surface coating of MgO. *Journal of Power Sources*, 88(2), pp.255-261.
- Lathrop, D.P., Fineberg, J. and Swinney, H.L., 1992. Transition to shear-driven turbulence in Couette-Taylor flow. *Physical Review A*, *46*(10), pp.6390-6405.
- Lee, M.H., Kang, Y.J., Myung, S.T. and Sun, Y.K., 2004. Synthetic optimization of Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O₂ via co-precipitation. *Electrochimica Acta*, 50(4), pp.939-948.
- Lee, S.W., Kim, H., Kim, M.S., Youn, H.C., Kang, K., Cho, B.W., Roh, K.C. and Kim, K.B., 2016. Improved electrochemical performance of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material synthesized by citric acid assisted sol-gel method for lithium ion batteries. *Journal of Power Sources*, 315, pp.261-268.
- Li, G., Yang, X. and Ye, H., 2015. CFD simulation of shear flow and mixing in a Taylor–Couette reactor with variable cross-section inner cylinders. *Powder Technology*, 280, pp.53-66.
- Liang, L., Du, K., Peng, Z., Cao, Y., Duan, J., Jiang, J. and Hu, G., 2014. Coprecipitation synthesis of Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ precursor and characterization of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material for secondary lithium batteries. *Electrochimica Acta*, *130*, pp.82-89.
- Liu, Y. and Fox, R.O., 2006. CFD predictions for chemical processing in a confined impinging-jets reactor. *AIChE Journal*, *52*(2), pp.731-744.
- Liu, L., Yang, X., Li, G., Huang, X. and Xue, C., 2020. Shear controllable synthesis of barium sulfate particles using lobed inner cylinder Taylor-Couette flow reactor. *Advanced Powder Technology*, 31(3), pp.1088-1099.

- Marchisio, D.L., Rivautella, L. and Barresi, A.A., 2006. Design and scale-up of chemical reactors for nanoparticle precipitation. *AIChE Journal*, 52(5), pp.1877-1887.
- Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of Ni-Rich hydroxide in reaction crystallization: Effect of Taylor vortex dimension and intensity. *Crystal Growth & Design*, 15(4), pp.1726-1734.
- Morales, J., Perez-Vicente, C. and Tirado, J.L., 1990. Cation distribution and chemical deintercalation of Li_{1-x}Ni_{1+x}O₂. *Materials Research Bulletin*, 25(5), pp.623-630.
- Ren, D., Shen, Y., Yang, Y., Shen, L., Levin, B.D., Yu, Y., Muller, D.A. and Abruña, H.D., 2017. Systematic optimization of battery materials: key parameter optimization for the scalable synthesis of uniform, high-energy, and high stability LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ cathode material for lithium-ion batteries. ACS Applied Materials & Interfaces, 9(41), pp.35811-35819.
- Serra, T., Colomer, J. and Casamitjana, X., 1997. Aggregation and breakup of particles in a shear flow. *Journal of Colloid and Interface Science*, 187(2), pp.466-473.
- Sun, Z., Jiao, L., Fan, Y., Li, F., Wang, D., Han, D. and Niu, L., 2016. Industrialization of tailoring spherical cathode material towards highcapacity, cycling-stable and superior low temperature performance for lithium-ion batteries. *RSC Advances*, 6(100), pp.97818-97824.
- Sung, M.H., Choi, I.S., Kim, J.S. and Kim, W.S., 2000. Agglomeration of yttrium oxalate particles produced by reaction precipitation in semi-batch reactor. *Chemical Engineering Science*, 55(12), pp.2173-2184.
- Thai, D.K., Mayra, Q.P. and Kim, W.S., 2015. Agglomeration of ni-rich hydroxide crystals in taylor vortex flow. *Powder Technology*, 274, pp.5-13.

- Wei, G.Z., Lu, X., Ke, F.S., Huang, L., Li, J.T., Wang, Z.X., Zhou, Z.Y. and Sun, S.G., 2010. Crystal habit-tuned nanoplate material of Li[Li1/3– 2x/3NixMn2/3–x/3]O₂ for high-rate performance lithium-ion batteries. *Advanced Materials*, 22(39), pp.4364-4367.
- Xu, L., Zhou, F., Kong, J., Chen, Z. and Chen, K., 2018. Synthesis of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ with sodium DL-lactate as an eco-friendly chelating agent and its electrochemical performances for lithium-ion batteries. *Ionics*, 24(8), pp.2261-2273.
- Yakhot, V., Orszag, S.A., Thangam, S., Gatski, T.B., Speziale, C.G., 1992.
 Development turbulence models for shear flow by a double expansion technique. *Physics of Fluids A: Fluid Dynamics*, 4(7), pp.1510-1520.
- Yang, C.K., Qi, L.Y., Zuo, Z., Wang, R.N., Ye, M., Lu, J. and Zhou, H.H., 2016. Insights into the inner structure of high-nickel agglomerate as highperformance lithium-ion cathodes. *Journal of Power Sources*, 331, pp.487-494.
- Ying, J., Wan, C., Jiang, C. and Li, Y., 2001. Preparation and characterization of high-density spherical LiNi_{0.8}Co_{0.2}O₂ cathode material for lithium secondary batteries. *Journal of Power Sources*, 99(1-2), pp.78-84.
- Ying, J., Jiang, C. and Wan, C., 2004. Preparation and characterization of highdensity spherical LiCoO₂ cathode material for lithium ion batteries. *Journal of Power Sources*, 129(2), pp.264-269.
- Yuan, J., Wen, J., Zhang, J., Chen, D. and Zhang, D., 2017. Influence of calcination atmosphere on structure and electrochemical behavior of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ cathode material for lithium-ion batteries. *Electrochimica Acta*, 230, pp.116-122.
- Yue, P., Wang, Z., Peng, W., Li, L., Chen, W., Guo, H. and Li, X., 2011. Spraydrying synthesized LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ and its electrochemical
performance as cathode materials for lithium ion batteries. *Powder Technology*, *214*(3), pp.279-282.

Zhu, Q., Xiao, H., Zhang, R., Geng, S. and Huang, Q., 2019. Effect of impeller type on preparing spherical and dense Ni_{1-x-y}Co_xMn_y(OH)₂ precursor via continuous co-precipitation in pilot scale: A case of Ni_{0.6}Mn_{0.2}Co_{0.2}(OH)₂. *Electrochimica Acta*, *318*, pp.1-13.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Hydrodynamically controllable synthesis of fine particles

The aim of this PhD work is to investigate the effects of the key hydrodynamic parameters on particle formation process in order to realize the controllable synthesis of fine particles by using various TC reactors. As a fundamental case study, barium sulfate was chosen as a model substance. The experimental parameter study of the preparation process of barium sulfate particles has been conducted, focusing on the initial supersaturation, reactant feeding rate, inner cylinder rotational speed (characterized by Reynolds number $Re = \frac{\omega dr_i}{v}$). The formation of fine aggregates based on crystallites, particle morphology, size and size distribution have been carefully observed in these designed experiments and the results obtained have been analysed. CFD modelling was also employed to assist the acquirement of the hydrodynamics such as shear induced turbulent energy dissipation rate, turbulent kinetic energy distribution and particle-eddy interactions occurring in the reactor, coupled with Lagrangian particle tracking to obtain the particle dispersion in the synthesis process. As an extension, the same modelling approach was also applied to the other reactive synthesis system, the preparation of NCM622 particles, an important precursor material for lithium ion batteries. The mixing of reactants in the TC reactor was comprehensively investigated. As the outcomes of the present studies, the main accomplishments of this project can be summarised as:

(1) Three different kinds of morphology of barium sulfate particles (i.e., flake, transition and granule) were produced by reactive precipitation in the LTC. The influence of the operating conditions, including the rotational speed of the inner cylinder, reactant feeding rate and initial supersaturation on the morphology transition have been examined. An empirical equation was proposed involving shear rate (rotational speed) and feeding rate. Such equation can be served as an indicator for morphology transition.

(2) The comparison of hydrodynamic characteristics between the CTC and LTC in terms of barium sulfate particle size, size distribution, and turbulence induced shear has indicated that the adoption of the LTC is effective to realise shear controllable synthesis of the particles with the desired properties due to the intensification of the turbulence eddy induced shear. A strong correlation between the synthesized particle size and the local turbulent dissipation rate has been identified.

(3) The experiments on the evaluation of micromixing efficiency in the TC reactor have been performed by using a parallel competing iodide-iodate reaction system. A relative small value of *Xs* under all tested conditions in the LTC suggests a good micromixing performance. This result is in an agreement with the CFD modelling result in terms of turbulent intensity. Micromixing time calculated according to the incorporation model is found to be the order of 10^{-5} s, much smaller than that of the conventional stirred tank reactor (2×10⁻³ to 2×10⁻² s).

(4) A large number of barium sulfate particles were tracked using Euler-Lagrange approach with consideration of the interfacial forces acting on the

particles. It has been revealed that the particle trajectories in both the CTC and LTC exhibit the behaviour of helical movement, being entrapped and strongly affected by Taylor vortices. Such interaction has reaffirmed the effect of turbulent shear in such reactors on the particle synthesis process, i.e. the control of particle properties due to the local turbulent eddies induced shear. Particle radial distribution indicates that there exists a separation strap of the particles inside and outside the vortices due to the different particle axial velocity, which can be used for particle classification. Particle axial dispersion coefficient presents a similar distribution curve to the particle size distribution, and the dispersion coefficient for the LTC is greater than that for the CLC. These results indicate more effective global mixing in the LTC than that in the CTC due to the enhanced deformation of Taylor vortices at the gap region of the LTC.

(5) The LTC was also successfully applied to the other reactive synthesis system, the preparation of NCM622 particles. Both CFD simulation and experiments were used for validation of the hydrodynamic characteristics of the synthesis process. The synthesized particle properties in terms of particle size, morphology and specific surface area by using the LTC are also found to be remarkably improved in comparison to the use of the CTC. This may be attributed to the enhanced shear rate in the impinging jet regions formed in the vicinity of the lobed inner cylinder surface for the LTC. Evaluation of the mixing between reactants has been made by implementing two user-defined scalars, $\bar{\xi}$ and $\bar{\xi'}^2$, revealing that better macromixing and micromixing can be more quickly obtained in the LTC than the CTC.

The specific realisations of the aforementioned claims are described in the following section.

7.2 Specific realizations

7.2.1 Synthesis of barium sulfate particles

The synthesis of the model substance, barium sulfate was firstly realised in the TC reactor (both the CTC and LTC). Both particle morphology and particle size have been assessed and studied in detail as reported in Chapters 2 and 3, respectively. The key parameters investigated include initial supersaturation, feeding rate, inner cylinder rotational speed (characterized by Reynolds number or shear rate). In Chapter 2, the interfacial phenomena in terms of particle morphology transition was studied in detail for the synthesis using the LTC. According to the SEM results, three different kinds of morphology are observed to take place, the outer-appearance of the shapes being classified as flake, transition and granule. It has been found that particle morphology transition is strongly dependent on the transition of flow patterns inside the LTC. At low concertation, particle morphology transition is observed to occur at the onset of turbulent Taylor-Couette flow, however, such morphology transition also appears at the onset of turbulent Taylor vortex flow at high concentration. It should be noted that the classification of flow patterns is based on Reynolds number $Re = \frac{\omega dr_i}{v}$, which can be changed by adjusting the rotational speed of the inner cylinder. It is also found that the formed particles exist in the form of agglomerate rather than single individual crystals. Both micromixing of reactants and mass transfer from bulk solution to the surface of the particle determine the final particle morphology. Subsequently, the mechanism of particle formation in such TC system has been proposed through examining the results by looking into the combined effects of both the rotational speed and feeding rate. An empirical correlating equation is thus presented for the

application of the cases of low initial supersaturation, yielding the quantitative description about the particle morphology. At a high supersaturation, it is found that particles are favourable to form granules due to the enhanced nucleation rate.

Starting from Chapter 2, a series of explorations to identify the TC reactor as a promising device for reactive precipitation of fine particles were conducted. In order to demonstrate the proposed LTC to have better performance than that of the traditional CTC, comparisons on the final products by using both reactors were also made. Thus, in Chapter 3, particle size and particle size distribution affected by hydrodynamic characteristics when using different types of inner cylinders under various operating conditions were particularly investigated. To reveal the impact of the hydrodynamics of Taylor-Couette flow due to the variation of the inner cylinder on the particles, CFD modelling was adopted. Before simulation, flow domain in the TC reactor was constructed by Design Modeller while the computational mesh was created by using ICEM, a mesh generation code embedded in ANSYS software. A sliding mesh method was adopted in the vicinity of the inner cylinder to circumvent the effect of irregular cross-section profile of the lobed geometry when the inner cylinder is rotating. The numerical calculation on hydrodynamics in the TC reactor was conducted by using FLUENT 17.0 as the experimental visualisations and observation on the particle synthesis in the TC reactor are still forbidden, especially for particle aggregation and the local turbulent eddies. Based on the results of SEM, XRD and simulated turbulence time and length scales, it is found that turbulent eddies may have little effect on crystallite formation process, but they may determine the final particle (or agglomerate) size and the size distribution as the turbulent eddies with the length scale down to the Kolmogorov scale will impose a strong

shear on the particle surface. It has been demonstrated that particle size is smaller, and the size distribution is narrower in the LTC with the increase of the inner cylinder rotational speed than those in the CTC. It should be noted here that the only difference between the CTC and LTC lies in the cross-sectional profile of the inner cylinder. The change in the inner cylinder cross-sectional profiles leads to the intensification of the impinging jet flows between the Taylor vortices in the LTC, which are formed between two typical counterrotating Taylor vortices. As a result, the velocity gradient in the radial direction increases, and the local turbulent shear is enhanced. A correlation between the synthesized particle size and the local turbulent dissipation rate (shear rate is a function of dissipation rate) was given with the change of sampling time to demonstrate the dependence of particle size on turbulent eddy induced shear. Sampling time can serve as a reference to indicate an appropriate time during particle preparation.

From the perspective of the preparation of barium sulfate particles, it is revealed that compared with the CTC, the use of the LTC can effectively improve the process of reactive precipitation through changing the turbulence induced shear strain rate distribution in the inwards and outwards impinging jet regions of Taylor vortices, which is beneficial to the formation of small particles with regular morphology and narrow size distribution. Turbulence generated not only has effects on final particles by exerting shear force on particle surface, but also determines the environment for chemical reaction. As chemical reaction takes place at the molecular level, mixing at the similar scale can directly influence its course. That means micromixing creates supersaturation, subsequently inducing chemical reaction. In order to quantitatively demonstrate the difference of the micromixing performance for the CTC and LTC, the trial reaction by employing the Villermaux iodide-iodate reaction system has been performed and the results are reported in Chapter 4. Several factors were examined by carefully collecting samples while the determination of sample collection time has been done in such a way to ensure the reliable UV results in principle. The acid concentration was also carefully chosen to avoid overloading, while the injection of acid was controlled to keep the feeding as slow as possible to eliminate the impact of the macromixing in the TC reactor. Comparing the value of segregation index, Xs, it is suggested that the hydrodynamic heterogeneity created by the LTC can significantly enhance micromixing efficiency. Moreover, the characteristic micromixing time, estimated by the incorporation model was calculated. Four ordinary differential equations were solved by the forth-order Runge-Kutta iteration. It is found that the micromixing time in the TC reactor is about three orders of magnitude lower than that of the conventional stirred tank reactor. Thus, when considering the enhancement of micromixing performance, alteration of the configuration of the inner cylinder would be an effective way for intensification of the process of particle preparation.

As a Taylor vortex and its typical structure determine the local hydrodynamic environment for particle formation, the dynamic interaction between Taylor vortices and the particles was studied in Chapter 5. In order to observe such interaction, barium sulfate particle trajectories based on the input for the simulation specified according to the actual properties of experimentally synthesized particles were tracked using Euler-Lagrange approach. Considering the TC reactor to be vertically installed, the buoyancy, drag and lift forces were considered to be dominant in the particle movement and thus implemented into the simulation. Also, in order to include the effect of turbulence on particle dispersion, stochastic tracking model was employed. By observing particle trajectories in the TC reactor, particle motion exhibits a helical movement, entrapped by Taylor vortices. Particles with high velocity magnitude tend to distribute in the large gap regions in the LTC, likely being attributed to the entrainment of particles by the impinging jet flows towards these regions, and the periodic gradually decrease gap for the LTC, where the flow in circumferential experiences an expansion following by a contraction. Particle or particle dispersion is significantly enhanced by increasing the inner cylinder rotational speed, and changing inner cylinder type from the CTC to LTC. In particular, velocity gradient in radial direction can bring out particle classification due to the difference in particle axial velocity. Particle axial dispersion can be seen as an indicator to characterise the global mixing. With the increase of the rotational speed, less time is needed for the particles to disperse a certain axial distance. Also, the calculated axial diffusion coefficient shows a similar distribution curve to the particle size distribution, and such coefficient for the LTC is greater and distribution is more even than those for the CLC, indicating that the local shear strain rate is enhanced due to the inner cylinder cross-sectional profile modification and more turbulent eddies are generated due to the periodic variation of gap size in the LTC. The results of particle tracking are consistent with the deduction as indicated in Chapter 3 that the utilisation of the LTC can effectively intensify the process of particle preparation.

7.2.2 Synthesis of NCM622 particles

Further study by employing the TC reactor was carried out both experimentally and numerically on the reactive system of co-precipitation of NCM622 particles.

As described in Chapter 6, the effects of processing time, inner cylinder type and the turbulent mean shear rate on particle preparation have been assessed and discussed. Processing time should be identified firstly, as this will provide the time scale for the products to reach a steady state. It is found that by employing the TC reactor, the processing time can be significantly reduced to 8 hours, which is much shorter than that by using the conventional stirred tank reactor with an estimation of at least 60 hours. For the comparison of inner cylinder types (i.e., CTC and LTC), the synthesised particle characteristics at various mean shear rates was characterized based on particle size, morphology and specific surface area. The diffraction peak intensity from the XRD measurement indicates the orientation of crystal growth under the influence of the local turbulent shear, where the peak intensity of planes (100) and (101) increases with the increase of the mean shear rate for the LTC. As for the change of particle size, particle size in the LTC is greater than that in the CTC. This difference may be attributed to the different turbulence induced shear features, which is characterised by Kolmogorov length scale turbulent eddies as the particles will interact with such turbulent eddies. For those particles with the size much smaller than the Kolmogorov length scale, turbulent eddies can enhance the entrapped particle collision, thus resulting in more particles aggregation to form large size particles. However, once the shear force caused by the turbulent eddy exerting on agglomerates exceeds the internal bonding force among the agglomerates, the size of agglomerated particles will be suppressed. Such effect becomes apparent in the LTC due to its periodic variation of gap size of the lobed inner cylinder.

Different from Chapter 4, which has evaluated the micromixing performance of the TC reactor, the mixing of the reactants assessed by two variables was carried

out in Chapter 6. The calculation of these two variables was implemented into the simulation by using UDS. Comparison was focused on the mean shear rate generated by the rotation of the inner cylinder in the CTC and LTC. It is revealed that the mixture fraction, $\bar{\xi}$, representing the mixing degree at macro sales, can take a shorter time to reach the required mixing condition for co-precipitation synthesis at a higher shear rate, especially for the LTC. The micro scale mixing, characterised by mixture faction variance, $\bar{\xi}'^2$ the key indicator to evaluate local supersaturation for molecular reaction, has a strong correlation with the turbulent energy dissipation rate. Such correlation can be seen as an indicator for the selection of different cross-sectional profiles of the inner cylinder in the TC reactor in order to obtain desired product characteristics.

7.3 Recommendations for future work

This PhD work has concentrated on one key issue, the effects of fluid dynamics on the course of fine particle preparation in the TC reactor by means of reactive precipitation, focusing on shear controllable synthesis of fine particles. Barium sulfate was chosen as a model particle to carry out the fundamental study. Then, the co-precipitation of NCM622 particles was also successfully achieved by using the TC reactor. The results obtained from particle quality, micromixing performance and hydrodynamics simulation, together with the particleturbulent eddy interaction can be used as a guidance for process intensification by means of the optimization of the reactor configuration, or the development of novel reactors. Although hydrodynamics has been explored in this project, there are still remaining many problems that need to be addressed in understanding the nature and the effects of the hydrodynamic heterogeneity

encountered in the TC reactor. Based on the accomplishment of present work, some recommendations for future work are summarised as follows:

(1) The flow field was simulated with the Reynolds Average Navier-Stokes (RANS) equations coupled with RNG k- ε turbulence model in current work. This means flow field information is presented with the mean value. However, chemical reaction coupled with mass transfer is dependent on the mixing at a micro scale which is generally smaller than the grid size. Also, the local turbulence structures still have not been resolved sufficiently by using such simulation approach, as eddies are assumed to be isotropic. In order to further understand and distinguish the inherent structures of turbulent eddies, large eddy simulation (LES) is suggested to be adopted as large eddies are resolved directly while isotropic small eddies can be modelled. Consequently, mixing can be better described at even small scale. However, LES requires finer meshes than those for RANS calculation and a long flow-time is needed to obtain the stable statistics, thus the computational cost is acceptably high. These shortcomings can be circumvented by improving the simulation capability.

(2) As for the simulation of particle trajectories, barium sulfate was treated as the spherical particle. The numerical simulation conducted is to realize the quantitative measurement of the particle dispersion on the effect of Taylor vortices embedded by small turbulent eddies. It has been recognised that the drag force experienced by the particles plays a leading role in determining the particle trajectories for the liquid-solid system especially when the density of the particles is much greater than that of the liquid. This is true in the present particle synthesis process. However, the assumption of spherical particle will bring certain deviation from the reality, especially for the case of the synthesised particles that present various shapes. For conducting more rigorous simulations, variation of the particle shapes should be taken into consideration. For an irregular shape of particle, shear stress and static pressure exerting on the particle surface are not evenly distributed, thereby the surface integral on these force contributions will give out different result comparing with a smooth surface spherical particle. For simplification, the final particle size distribution obtained from the experimental observations can be reasonably used at the onset of particle injection from the inlet, served as the boundary condition for the simulation of particle dispersion in the TC reactor. However, further work on the correction of the drag law equation and particle size changing with time is suggested to be realised in the numerical simulation of the particle dispersion, which can be achieved by adopting the user-define function (UDF) in ANSYS Fluent code.

(3) It has been denoted in Chapter 6, final cathode material, LiNCM622 can inherit the morphology and structure from NCM622 precursor. Only NCM622 particles have been concerned in this PhD work. The experimental work is the first step in understanding the mechanism of turbulent eddy-particle interaction. Subsequent studies including calcination, characterization of electrochemical performance, and surface modification are still necessary for the establishment of a complete system of the cathode material formation. Also, for a theoretical investigation, simulation based on molecular behaviour is strongly suggested, which enables the visualization of working mode of the lithium ion batteries, such as lithium ion diffusion, phase transition of crystal growth, and temperature distribution.

(4) For a multi-phase reactive system, the interaction between liquid and solid has been involved in this work. However, there are still some inadequacies which need to be circumvented, so that the reactive precipitation coupling with hydrodynamic effect on the course of fine particle preparation can be fully captured. For example, chemical reaction with detailed kinetics is suggested to be involved into the simulation, which can be realised by solving species transport, where the species can be defined as the reactant concentration or the relevant parameter which is closely related to the mass transfer in the synthesis of the fine particles. Moreover, the effect of turbulent eddies on particle agglomeration is another important factor during crystallization, which is suggested to be considered in the simulation. This process can be realised by using the population balance model (PBM) by taking agglomeration kinetics, collision caused by turbulent eddy motion and Brownian motion into consideration. In order to validate such effect, modelling results can be further compared and corrected according to the current experimental results of particle size distribution. Although such reactive precipitation system is complicated and challengeable to be simulated due to the complicated coupling of many parameters and high computational cost, it would be much beneficial to implement chemical reaction kinetics into the current two-phase modelling, which will provide the physical insight into the effects of hydrodynamics on the overall process of reactive precipitation, thereby completely modelling the sophisticated controllable synthesis system.

LIST OF PUBLICATIONS

Journal articles

- Liu, L., Yang, X., Li, G., Huang, X. and Xue, C., 2020. Shear controllable synthesis of barium sulfate particles using lobed inner cylinder Taylor-Couette flow reactor. *Advanced Powder Technology*, 31(3), pp.1088-1099.
- Guo, Y., Yang, X., Li, G., Yang, J., Liu, L., Chen, L., and Li, B., 2021. Shear Turbulence Controllable Synthesis of Aggregated Nano-Particles Using a Swirling Vortex Flow Reactor Assisted by Ultrasound Irradiation. *Chemical Engineering Journal*, 405, 126914.

Major revision

- Liu, L., Yang, X., Yang, J., Li, G., and Guo, Y., 2020. Modelling of turbulent shear controllable coprecipitation synthesis of lithium ion battery cathode precursor micro-particles in a Taylor-Couette flow reactor with variable configurations of inner cylinder. (submitted to *Chemical Engineering Journal*).
- Liu, L., Yang, X., Yang, J., Li, G., and Guo, Y., 2020. Effect of hydrodynamic heterogeneity on micromixing intensification in a Taylor-Couette flow reactor with variable configurations of inner cylinder. (submitted to *AIChE Journal*).

Under review

Liu, L., Yang, X., Yang, J., Li, G., and Guo, Y., 2020. Effect of hydrodynamic heterogeneity on particle aggregate dispersion in a Taylor-Couette flow reactor with variable configurations of inner cylinder. (submitted to *Powder Technology*).

Book chapter

Liu, L., Li, G., Yang, X., Huang, X. and Xue, C., 2019. Interfacial Phenomena in the Synthesis Process of Barium Sulfate Particles Precipitated in a Lobed Inner Cylinder Taylor-Couette Flow Reactor: Effects of Fluid Dynamics. In *Wettability and Interfacial Phenomena-Implications for Material Processing*. IntechOpen.