Tsinghua University
Academic Works
清华大学学术专著

Multi-Phase Chemical Reaction Engineering and Technology (Part Ⅰ)

多相化学反应工程与工艺（上）

Editors: Yong JIN, Fei WEI
金涌　魏飞　主编

Tsinghua University Press
清华大学出版社

内 容 简 介

本书是清华大学化工系反应工程方面的集成之作。本书内容包括：流态化科学与工程方面的研究进展，与多相反应工程和工艺相关的粉体、造粒、绿色化工和生态工业等前沿领域的新内容和新进展，以及能源与环境等涉及可持续发展的战略问题，这对开发清洁能源技术，发展绿色化工和生态工业具有重要的意义。本书还涉及多相反应工程的先进的研究和数据处理方法。

本书可供化工、材料、能源等领域的科研工作者和高校相应专业的师生参考。

图书在版编目（CIP）数据

多相化学反应工程与工艺 / 金涌，魏飞主编. —北京：清华大学出版社，2006.6

（清华大学学术专著）

ISBN 7-302-12506-6

I. 多…　II. ①金…　②魏…　III. 多相催化–化学反应工程　IV. TQ032.41

中国版本图书馆 CIP 数据核字（2006）第 013162 号

出 版 者：清华大学出版社　　**地　　址**：北京清华大学学研大厦

http://www.tup.com.cn　　**邮　　编**：100084

社 总 机：010-62770175　　**客户服务**：010-62776969

责任编辑：黎　强

印 刷 者：清华大学印刷厂

装 订 者：三河市春园印刷有限公司

发 行 者：新华书店总店北京发行所

开　　本：185×260　**印张**：61　**字数**：1518 千字

版　　次：2006 年 6 月第 1 版　2006 年 6 月第 1 次印刷

书　　号：ISBN 7-302-12506-6/TQ・26

定　　价：150.00 元（上、下册）

Yong JIN

Professor, Department of Chemical Engineering, Tsinghua University; Member of CAE (Chinese Academy of Engineering).

JIN was born in Beijing in 1935. He got his bachelor degree of chemical engineering in Ural Polytechnic College (Russia) in 1959 and studied graduate courses of chemical engineering in Tianjin University from 1959 to 1960. He became an assistant professor of University of Science and Technology of China in 1960. Since 1973, he had been working in Tsinghua University. As a visiting scholar, he engaged in chemical reaction engineering in Pittsburgh University of USA in 1985. His speciality is fluidization reaction engineering, coupling technology in chemical process, environmental friendly chemical process, particle coating and surface modification, cycle economy and ecological process engineering. As a first contributor, he had received many important national s awards of science and technology, including National Science & Technology Advancement Award, and National Invention Award.

Fei WEI

Professor, director of Beijing Key Laboratory of Green Chemical Reaction Engineering & Technology at Tsinghua University.

WEI was born in He'nan in 1962. He obtained his bachelor degree of chemical engineering in University of Petroleum (China) in 1984, and got his master and Ph.D. at University of Petroleum (China) in 1987 and 1990. Since 1990, he had been working in Tsinghua University. He had been the visiting professor in Ohio State University on multiphase reactor in 1999. His research field is multiphase reactor and nano-material manufacture. Prof. WEI has won many honors and awards, such as, National Science & Technology Advancement Award, the National Scientific Award for Outstanding Youth (1996), and the Chinese Particuology Award for Youth (1997). He was honored as Cheung Kong Scholar of the Ministry of Education in 1999. He has more than 100 journal published papers and patents.

Preface

For the past three decades, the Fluidization Laboratory of Tsinghua University (FLOTU) has been one of the leading research and development groups in the world working on the fundamentals and applications of fluidized beds and a wide range of related technologies. Under the dynamic leadership of Professor Jin Yong, ably assisted in the early years by Professor Yu Zhiqing and more recently by Professor Fei Wei, many innovations and advances have been realized, addressing challenges in a wide range of areas. It is an honour for me to have an opportunity to prepare this Preface for a volume summarizing the advances and achievements of this excellent group.

The first section of this volume addresses Downers, reactors where particles travel downwards co-currently with gas. No other group in the world has been as active as FLOTU in performing fundamental research to understand the flow patterns of downers, mixing phenomena, practical configuration issues and modelling. Thanks to their efforts, downers are now considered seriously as alternative reactors with potential advantages for a number of industrial reactions. The group has also pioneered novel riser-downer combinations with the potential to combine the advantages of both risers and downers.

Section 2 covers the extensive research performed by the Tsinghua group on gas-solid risers. Risers are widely used in industry for catalytic and non-catalytic gas-solid reactions. Their adoption has been greatly facilitated by the wide-ranging research efforts of this group. Among other achievements, they were among the first groups to recognize the importance of exit configurations, the first to measure gas velocity profiles accurately, and one of the first to measure suspension-to-surface heat transfer coefficients. Their pioneering work using phosphorescent tracer particles has elucidated flow patterns in circulating fluidized beds. They have also been innovative in exploring a range of novel geometries, and in modelling a number of reactor configurations in which risers are featured.

The FLOTU group has also contributed to the understanding of fluidized beds operated in the bubbling and turbulent fluidization flow regimes. Section 3 features work in these areas. Once again this work is characterized by careful attention to detail coupled with imagination and diligence. For example, unique pagoda-shaped baffles have been shown to have attractive characteristics for improving the quality of fluidization. The transition from bubbling to turbulent fluidization has been elucidated in a series of interesting papers.

The following section covers an extensive array of studies in which the FLOTU group has contributed to the fundamentals and applications of two- and three-phase systems where liquid constitutes one of the phases. The group has done pioneering work to extend the concept of circulating fluidized beds to liquid-solid and gas-liquid-solid systems. Innovative work has also been reported on clever multi-phase contactors with internal baffles and external loop airlift. In each of these cases, the group has demonstrated its ability to make complex multi-phase flow equipment function, overcoming practical limitations encountered by previous research groups. This body of work is essential reading for those seeking clever ways of reconfiguring mass transfer equipment and reactors for a wide range of multi-phase processes.

The general theme of novel configurations for multiphase reactors and contactors is extended in the next section of this book to cover systems where moving packed beds are advantageous. This work, applied to reactors, hoppers and standpipes, again provides new insights and innovative concepts for dealing with flow, mixing and contacting in practical particulate and multi-phase systems.

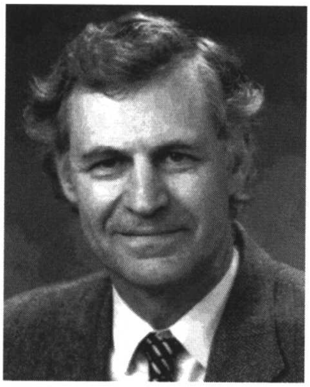
Section 6 demonstrates that this group is capable not only of fundamental work and clever design, but that it has also pioneered a number of unusual technologies for particular applications. Of special interest is the work combining fundamentals and applications related to nano-particles. Special reactor configurations have been devised to optimize these processes, for example a two-stage fluidized bed reactor for simultaneously producing hydrogen and carbon nano-tubes.

Mindful of the responsibility of engineers and scientists to preserve and strengthen the planet for future generations, Professor Jin and his colleagues have recently turned their attention to what is being called "Green Engineering and Technology." Not content to just think about or write about the implications of resource over-utilization, climate change and narrow technical approaches, the FLOTU group offers a series of processes in section 7, in which it is demonstrated that the coupling of seemingly unrelated processes or concepts can have synergetic economic and environmental benefits. The volume closes with a thoughtful and mature essay where the authors consider the ecological context of chemical engineering work. This forward-looking piece sets a high standard and demonstrates the importance of engineers recognizing that their work has consequences extending well beyond the narrow context in which they usually work in industry, academia and government.

Many of the papers collected here have appeared in sources not readily accessible to the scientific community in the west due to language and publishing restrictions. This volume offers a truly impressive and exciting array of contributions that challenge the reader and demonstrate the breadth and quality of this truly excellent and unique research group.

John R. Grace
Professor and Canada Research Chair
University of British Columbia,
Vancouver, Canada

John Ross Grace



Director, Fluidization Research Centre (FRC)
Fellow, Engineering Institute of Canada
Fellow, Canadian Academy of Engineering
Fellow, Chemical Institute of Canada
Fellow, Royal Society of Canada

Dr. Grace is a Professor in the Department of Chemical and Biological Engineering at the University of British Colombia. Dr. Grace is an outstanding Canadian figure in Chemical Engineering. He is the author of approximately 260 articles and book chapters and coauthor of the leading book *Bubbles, Drops and Particles*, published in 1978. His primary research interests are concerned with fluidized bed reactors and related multi-phase systems. Throughout his career, Dr. Grace has received many awards and acknowledgments and is presently the holder of a Canada Research Chair.

List of Common Symbols

a	average activity in a particle (catalyst)
A	Hamaker constant, J
A_0	reactor cross-section area, m^2
A_p	surface area of the particle, m^2
Ar	Archimedes number
Bo	Bodenstein number
C	concentration of tracer, kg/m^3
C_A or c_A	concentration of A, mol/m^3
C_d	drag force coefficient between particles and gas
C_{ds}	drag force coefficient between a single particle and gas
C_D	trag coefficient
d_p	particle diameter, m
d_s	mean diameter of particle, m
D	reactor diameter, m
D	distribution factor
D_{AB}	diffusion coefficient, m^2/s
D_{as}	axial particle dispersion coefficient, m^2/s
D_{rs}	radial particle dispersion coefficient, m^2/s
$(dp/dl)_s$	pressure gradient in the standpipe, Pa/m
e	restitution coefficient
e	dissipation rate of turbulent kinetic energy of gas phase, m^2/s^3
F_c	interparticle attractive force, N
F_d	drag force on particle, N
F_D	drag force, N/m^3
F_f	friction between fluid (particle) and wall, N/m^3
F_g	effective weight of particle, N
Fr	Froude number
g	gravitational acceleration, $g = 9.8\ m/s^2$
G or G_s	solids flux, $kg/(m^2 \cdot s)$
h or H	distance to downer entrance or height of fluidization bed, m
h	heat transfer coefficient, $W/(m^2 \cdot K)$
k	turbulent kinetic energy, m^2/s^2
k_a	reaction rate constant, s^{-1}
k_d	deactivation rate constant, $m^3/(mol \cdot s)$

k_m	reaction rate constant, m^3/ (kg • s)
K_A	reaction rate constant, kmol/(kgcat • s)
L	length of the first accelerating zone, m
m	phase ratio
m_s	mass flow rate, kg/s
M_A	molecular weight of product A, kg/kmol
M_B	molecular weight of product B, kg/kmol
n	reaction order
p	pressure, Pa
Pe	Peclet number
Q	flow feed or gas flowrate, m^3/s
r	radial position or radial coordinate, m
r_A	reaction rate , kmol/(kgcat • s)
r/R	dimensionless radial position
R	universal gas constant, $R = 8.314$ J/(mol • K)
R	radius of downer or riser, m
Re	Reynold number
S_{par}	swirling-to-primary air ratio
Sc	Schmidt number
Sh	Sherwood number
t	reaction time, s
T	temperature, K
u_{mb}	superficial fluid velocity at incipient bubbling, m/s
u_g	superficial gas velocity, m/s
u_{gs}	superficial gas-splitting velocity based on the cross-section area of the standpipe, m/s
u_{slip}	velocity of the liquid and solid, m/s
u_{mf}	incipient fluidization velocity of the particles or superficial fluid velocity at incipient fluidization, m/s
u_t	terminal particle velocity, m/s
v	velocity, m/s
v_p	axial particle velocity, m/s
V	volume of liquid in the reactor, m^3
V_{total}	total gas flux, m^3/h
w	weight of the catalyst, kg
w_p	weight of the catalyst particle, kg
W_T	mass flow rate of gas, kg/s
x	length from the reactor inlet, m
y_A	weight fraction of substance A in the mixture
Y	ratio of volumetric flowrate of bubbles and excess gas flowrate

z	height of fluidization bed or axial coordinate, m
Z	surface distance between particles, m

Subscripts

0	initial value
f	fluid
g	gas phase
l	liquid phase
p	particle
s	solid phase
cat	catalyst (appear in physical units too)
cal	calculated
dil	dilute
exp	experimental
in	inlet
sus	suspension flow
t	turbulence
w	wall

Greek letters

ε	bed voidage
ε_s	solid holdup
ε_{mf}	voidage at incipient fluidization
λ_f	total friction coefficient between gas-particle and wall
λ_g	friction coefficient between gas and wall
ρ	density, kg/m^3
η	effectiveness factor of internal diffusion in the catalyst
μ	viscosity, Pa • s
μ_L	viscosity of liquid , Pa • s
α, θ	angle
Δp_t	total pressure drop, Pa
$\Delta p_{t,max}$	maximum total pressure drop, Pa
ΔE	reaction activation energy, J/mol
ΔE_d	deactivation activation energy, J/mol
β_w, β_d	fraction of solids carried up by a bubble within its wake and drift

Contents

1 Gas-Solid Cocurrent Down-Flow Fluidized Beds (Downers)

1.1 Hydrodynamics of downers

1.1.1 State-of-the-art review of downer reactors

1.1.1.1 Introduction

In the last two decades, considerable progress has been made in developing and applying riser reactors as an efficient gas-solids reactor. On the one hand, riser reactors offer significant advantages over conventional bubbling fluidized bed reactors, such as high gas-solids contact efficiency, high gas and solids throughput and the ability to handle cohesive particles. On the other hand, they may suffer from severe solids backmixing due to non-uniform gas and solids flow. Especially in residual oil catalytic cracking, it would be advantageous to have short residence time (less than 1.0 s) with narrower residence time distributions and flow pattern closer to the ideal plug flow.

The disadvantages of the riser reactor caused by the hydrodynamic effects of both gas and solids flowing against gravity, may be overcome in a new type of chemical reactor-downer reactor, in which the flow direction of both the gas and the solids are downwards in the same direction as gravity. In this paper, the flow mechanism, hydrodynamics, mixing, numerical simulation and applications of downer reactor are addressed.

1.1.1.2 Brief history

In the early 1970s, Stone and Webster began to develop a new type of reactor, mainly consisting of a solids-gas feed mixer, a downflow reactor section and a specially designed gas-solids separator[1,2]. This reactor is reported to offer very short residence times (~200 ms), near plug flow and a high temperature reaction environment. Applying the same principle, an ultra-rapid fluidized bed reactor was proposed for biomass pyrolysis[3,4]. To respond to potential industrial applications of downer reactors, researchers have begun to be interested in the fundamental study and applications of downers. Table 1 lists reported studies on downer reactors according to research topic considered in the last decade. Principal experimental methods are listed in Table 2. It can be seen that in the recent years more and more techniques have been adopted to investigate various aspects of downer reactors, such as the hydrodynamics, gas-solids mixing behavior and heat transfer. All these efforts greatly enhance the knowledge of downer reactors and are beneficial to industrial applications.

Table 1 Research on downer reactors

Research regime		Literature list
Overall flow behavior		[4–10]
Hydrodynamics	Flow section and axial profiles	[11–16]
	Radial profiles	[11,12, 14–21]
Mixing and transfer behavior		[22–30, 8]
Transient analysis and cluster		[31–35]
Distributor and entrance region		[25,13,36–40,8,10,34]
Modeling		[41–46]
Reactor applications		[47–51,3,42]

Table 2 Experimental methods in the research on downer reactors

Experimental methods	Applications	Literature list
Aspirating probe device	Local solid flux	[9]
Capacitance sensor	Local solids density	[16,32]
Fiber-optic probe	Local particles velocity, solids density, clustering phenomena	[17,12,25,31,45,14,15,33,19]
Helium or hydrogen tracer	Gas dispersion	[24,30]
LDV sensor	Local particle velocity	[6,12,18]
Miniature cylindrical heat transfer probe, heat flux probe	Heat transfer coefficients	[28,27]
Phosphoresent particle tracers	PTD of particles, radial and axial mixing behavior	[22–24,52,26]
Thermal method measuring temperature changes	Contact efficiency between gas and solids	[39]
X-ray or gamma-ray tomography	Local solids density	[37,38,16]
X-ray imaging	Local solids density	[9]

1.1.1.3 Applications

(1) FCC and heavy oil cracking

Short contact time and plug flow are desirable for catalytic cracking of heavy oil. In practical applications, downers have potential for this application(see Fig. 1). In 1993, UOP ran a down-flow short contact commercial reactor, called MSCC with 5% increase of yield. Figs. 2 and 3 show results from small hot model test unit run under typical conditions for FCC and deep catalytic cracking (DCC) processes in comparison with riser reactors. It is shown that the yield of gasoline increased by more than 5%, while the dry gas and coke decreased by more than 5% by switching to a downer reactor. At the same time, a number of patents have been applied as shown in Fig. 4[53,10].