

# Contents

**Preface — XV**

**About the authors — XXI**

## **Part A: Multiphase reactors: chemical reaction engineering**

### **1 Introduction — 3**

- 1.1 Book introduction — 3
- 1.2 A reaction engineer meets an electronic engineer — 5
- 1.3 Levenspiel's genius Problem 1.1 — 5
- 1.4 A short history of chemical reaction engineering — 10
  - 1.4.1 Introduction — 10
  - 1.4.2 Birth of chemical reaction engineering — 10
  - 1.4.3 Founding fathers of CRE — 12
  - 1.4.4 CRE as a language game — 13
  - 1.4.5 Dimensionless numbers in CRE: the persons behind the number — 13
- 1.5 Reaction engineering as introduction to process design — 17
- 1.6 Exercises — 17
- 1.7 Takeaway learning points — 18
  - References — 18

### **2 Overview of multiphase reactors — 20**

- 2.1 Introduction — 20
- 2.2 Two-phase G-S reactors — 22
  - 2.2.1 Fixed bed reactors — 22
  - 2.2.2 Gas-solid fluid bed reactors — 24
- 2.3 Two-phase G-L and L-L reactors — 31
  - 2.3.1 Gas-liquid bubble column reactors — 31
  - 2.3.2 Continuous and batchwise operation — 33
  - 2.3.3 Mechanically stirred gas-liquid reactors — 34
  - 2.3.4 Gas-liquid spray tower reactor and Venturi washer — 35
  - 2.3.5 Gas-liquid packed bed reactor — 37
  - 2.3.6 Two-phase L-L reactors — 38
- 2.4 Three-phase gas-liquid-solid reactors — 40
  - 2.4.1 Slurry reactors (liquid is continuous phase) — 40
  - 2.4.2 Trickle-bed three-phase reactor with gas as the continuous phase — 41
- 2.5 Reactors with heat control — 43
  - 2.5.1 Introduction of reactors with heat control — 43
  - 2.5.2 Adiabatic heat control — 44

2.5.3	Multitubular fixed bed reactor —	<b>44</b>
2.5.4	Wall (jacket) heat exchange —	<b>45</b>
2.5.5	Heat transfer by evaporation and a condenser —	<b>45</b>
2.5.6	Heat transfer by coils inside the reactor —	<b>45</b>
2.5.7	Microwaves heating —	<b>45</b>
2.5.8	Electrical heating —	<b>45</b>
2.6	Exercises —	<b>46</b>
2.6.1	Industrial exercise 1: reactor types for PVC depolymerization start-up company —	<b>46</b>
2.6.2	Industrial exercise 2: reactor type options for precipitation reaction —	<b>46</b>
2.7	Takeaway learning points —	<b>47</b>
	References —	<b>47</b>

## **Part B: Fundamentals**

<b>3</b>	<b>Scale-independent basics relevant for all reactors —</b>	<b>51</b>
3.1	Reaction stoichiometry and kinetics —	<b>51</b>
3.1.1	Introduction —	<b>51</b>
3.1.2	Reaction stoichiometry —	<b>51</b>
3.1.3	Definition of reaction rate and kinetics —	<b>53</b>
3.1.4	Reaction rate equations —	<b>55</b>
3.1.5	Experimental kinetics determination —	<b>59</b>
3.2	Reactor performance definitions —	<b>60</b>
3.2.1	Process and reactor boundaries —	<b>60</b>
3.2.2	Reactor conversion —	<b>61</b>
3.2.3	Integral versus differential reactor selectivity —	<b>62</b>
3.2.4	Reactor production capacity —	<b>64</b>
3.2.5	Process conversion and yield —	<b>64</b>
3.2.6	Definitions of terms: space velocity, GHSV, WHSV, LHSV —	<b>65</b>
3.2.7	Residence time and space time —	<b>67</b>
3.2.8	Limiting reactant —	<b>67</b>
3.3	Physical properties —	<b>68</b>
3.3.1	Reaction medium density modeling —	<b>68</b>
3.3.2	Physical transport properties —	<b>69</b>
3.4	Reaction enthalpy —	<b>69</b>
3.5	Reaction runaway behavior —	<b>70</b>
3.5.1	Example from Jan's experience —	<b>71</b>

3.6	Exercises —	72
3.7	Takeaway learning points —	73
	References —	73
	List of symbols —	74
<b>4</b>	<b>Residence time distribution and mixing theory —</b>	<b>75</b>
4.1	Residence time distribution theory —	75
4.2	The plug flow reactor concept: PFR —	78
4.3	The perfectly backmixed reactor: CSTR or CISTR —	79
4.4	Intermediate macromixing —	81
4.4.1	Tanks-in-series concept —	81
4.4.2	Axial dispersion concept —	82
4.5	Residence time distribution effects on conversion/selectivity —	84
4.6	Micromixing, earliness of mixing and segregation —	88
4.6.1	Earliness of mixing —	89
4.6.2	Degree of segregation —	91
4.6.3	Takeaway messages: macro- and micromixing —	93
4.6.4	Application of RTD theory to ideal reactor type selection —	94
4.7	RTD of real reactors —	94
4.7.1	RTD of two- and three-phase fixed bed reactors —	94
4.7.2	Residence time distribution G-L bubble columns —	98
4.7.3	Bubbling fluid bed residence time distributions —	100
4.7.4	Residence time distribution G-L-S bubble columns and fluid beds —	101
4.8	Exercises —	102
4.8.1	Industrial exercise 1: RTD of a new reactor for a new process —	102
4.8.2	Industrial exercise 2: fresh coconut drying in a fluid bed —	103
4.8.3	Industrial exercise 3: catalyst deactivation in a three-phase slurry reactor —	105
4.9	Takeaway learning points —	107
	References —	107
<b>5</b>	<b>Inter- and intraphase mass and heat transfer —</b>	<b>109</b>
5.1	Introduction to mass transfer —	109
5.1.1	Mass transfer from gas phase to liquid phase to porous solid phase —	110
5.2	Concept of transfer coefficients —	110
5.3	Multiphase mass and heat transfer: inter- and intraphase effects —	112
5.3.1	Exercise: mass transfer in series and/or in parallel —	112
5.4	Mass transfer with reaction in gas-liquid reactors —	113
5.4.1	Introduction —	113
5.4.2	Chemical enhancement and the Hatta number —	113
5.5	Mass transfer in heterogeneous catalysis —	116

5.5.1	Introduction —	<b>116</b>
5.5.2	Diffusion in porous catalysts —	<b>118</b>
5.5.3	Consequences for catalyst performance —	<b>120</b>
5.5.4	Effect on catalyst activity: Thiele modulus and the concept of effectiveness factor —	<b>120</b>
5.5.5	Effect on apparent reaction orders —	<b>126</b>
5.5.6	Effect on apparent activation energy —	<b>127</b>
5.5.7	Effect of particle size and fluid velocity —	<b>129</b>
5.5.8	Pore diffusion and catalyst design in terms of size and shapes —	<b>130</b>
5.5.9	Example: the periodic table of the trilobes —	<b>131</b>
5.6	Exercises —	<b>134</b>
5.6.1	Industrial exercise 1: catalyst particle size and shape for the dehydration of MPC —	<b>134</b>
5.6.2	Industrial exercise 2: diffusion and deactivation for bimodal pore size distribution —	<b>135</b>
5.7	Takeaway learning points —	<b>138</b>
	References —	<b>138</b>
<b>6</b>	<b>Quantification of mass transfer in G-L(-S) reactors —</b>	<b>140</b>
6.1	Introduction —	<b>140</b>
6.2	Mass transfer coefficients and Sherwood numbers —	<b>141</b>
6.3	Quantified mass transfer two- and three-phase bubble columns —	<b>142</b>
6.3.1	Gas-liquid mass transfer in horizontal bubble columns —	<b>143</b>
6.3.2	Liquid-solid mass transfer in three-phase bubble columns —	<b>144</b>
6.3.3	Shear rate distribution commercial scale on bubbles and droplet size distribution —	<b>144</b>
6.3.4	Particle (catalyst) breakage and attrition —	<b>145</b>
6.4	G-L-S mass transfer in trickle-bed reactors —	<b>145</b>
6.5	Process intensification methods for interface transfer —	<b>147</b>
6.5.1	Rotating reactors —	<b>147</b>
6.5.2	Other process intensified reactors —	<b>148</b>
6.6	Exercises —	<b>148</b>
6.7	Takeaway learning points —	<b>149</b>
	References —	<b>149</b>
<b>7</b>	<b>Heat management —</b>	<b>151</b>
7.1	Introduction —	<b>151</b>
7.2	Theory nonisothermal behavior reactors —	<b>151</b>
7.2.1	Nonisothermal backmixed reactor —	<b>153</b>
7.2.2	Nonisothermal tubular reactor —	<b>156</b>
7.2.3	Reactor design to avoid temperature runaway —	<b>157</b>

- 7.2.4 Quantified heat transfer for two- and three-phase slurry and fluid bed reactors — **161**
- 7.2.5 Mechanically stirred reactor heat transfer — **164**
- 7.3 Reactor operation and dynamic behavior — **164**
- 7.4 Exercises — **166**
- 7.5 Takeaway learning points — **166**
- References — **166**

## **8 Multiphase reactor modeling — 168**

- 8.1 Introduction — **168**
- 8.2 Models for and two- and three-phase fixed bed reactors — **170**
  - 8.2.1 Adiabatic versus nonadiabatic — **170**
  - 8.2.2 Pseudo-homogeneous models — **171**
  - 8.2.3 Heterogeneous models — **174**
  - 8.2.4 CFD models — **175**
- 8.3 Models for trickle-bed reactors — **176**
  - 8.3.1 Co-current trickle-bed — **176**
  - 8.3.2 Adiabatic trickle-bed — **176**
  - 8.3.3 Multitubular heat exchange trickle-bed — **176**
  - 8.3.4 Countercurrent trickle-bed flow — **176**
- 8.4 Models for bubble columns — **177**
  - 8.4.1 Models for G/L bubble columns — **177**
  - 8.4.2 CFD models for G/L/S (slurry) bubble columns — **177**
- 8.5 Models for fluid beds — **178**
  - 8.5.1 Models for G/S fluid beds — **178**
  - 8.5.2 CFD models for L/S fluid beds — **178**
  - 8.5.3 CFD models for three-phase mechanically stirred fed-batch reactors — **178**
- 8.6 Exercises — **179**
- 8.6.1 Industrial exercise 1: trickle-bed reactor — **179**
- 8.7 Takeaway learning points — **179**
- References — **180**

## **Part C: Stage-gate innovation methods**

### **9 Stage-gate innovation methods — 183**

- 9.1 Introduction — **183**
- 9.2 Innovation stages overview — **184**
  - 9.2.1 Discovery stage — **184**
  - 9.2.2 Concept stage — **184**
  - 9.2.3 Feasibility stage — **184**

9.2.4	Development stage —	185
9.2.5	Engineering procurement construction stage —	185
9.2.6	Operation stage —	185
9.2.7	Abandon stage —	185
9.3	Takeaway learning points —	185
	References —	186
<b>10</b>	<b>Multiphase reactor selection —</b>	<b>187</b>
10.1	Introduction —	187
10.2	Critical review some academic methods reactor selection —	187
10.2.1	Reactor family tree selection —	187
10.2.2	Three-level multiphase reactor selection method —	188
10.3	Reactor selection method when scale-up risk is low for reactor types considered —	189
10.4	Introduction to industrial reactor selection and its practice —	189
10.4.1	Introduction —	189
10.4.2	Ideation stage reactor type selection —	192
10.4.3	The power of reactor selection in the ideation stage: Shell shale fluid bed case —	193
10.5	Reactor type selection in the various innovation stages —	195
10.5.1	Concept phase reactor selection —	195
10.5.2	Feasibility stage reactor selection —	198
10.5.3	Development stage front-end engineering design reactor selection —	202
10.5.4	Engineering procurement construction (EPC) stage reactor selection —	202
10.6	Exercises —	203
10.6.1	Industrial exercise 1: reactor type selection in ideation stage —	203
10.6.2	Industrial exercise 2: reactor selection concept stage —	203
10.6.3	Industrial exercise 3: reactor family-type selection ideation stage —	204
10.7	Takeaway learning points —	205
	References —	205
<b>11</b>	<b>New reaction systems through all innovation stages —</b>	<b>206</b>
11.1	Introduction —	206
11.2	Ideation stage (also called discovery stage, or early research stage) —	206
11.2.1	Ideation stage design —	206
11.2.2	Ideation stage modeling —	207
11.2.3	Ideation stage proof of principle experiments —	207
11.3	Concept stage (also called research stage) —	207
11.3.1	Concept design —	207

11.3.2	Concept modeling —	<b>211</b>
11.3.3	Experimental validation —	<b>211</b>
11.4	Feasibility stage design (also called first part of development stage) —	<b>212</b>
11.4.1	Introduction —	<b>212</b>
11.4.2	Reactor development plan overview —	<b>212</b>
11.4.3	Critical performance factors for commercial-scale reactors —	<b>213</b>
11.4.4	Reactor scale-up methods and applications —	<b>216</b>
11.4.5	Cold flow test rigs —	<b>223</b>
11.5	Development stage —	<b>224</b>
11.5.1	Introduction —	<b>224</b>
11.5.2	Pilot plant and test program execution —	<b>224</b>
11.5.3	Front-end engineering design —	<b>224</b>
11.6	Engineering, procurement, and construction (EPC) stage (also called execution stage) —	<b>226</b>
11.6.1	Contractor choice and co-operation —	<b>226</b>
11.6.2	Reactor procurement and construction —	<b>227</b>
11.6.3	Commissioning —	<b>227</b>
11.7	Start-up and normal operation (also called demonstration stage) —	<b>227</b>
11.8	Exercises —	<b>228</b>
11.8.1	Industrial exercise: glucose to ethylene glycol —	<b>228</b>
11.9	Takeaway learning points —	<b>229</b>
	References —	<b>230</b>

## Part D: Education

<b>12</b>	<b>Education guidelines —</b>	<b>235</b>
12.1	Introduction —	<b>235</b>
12.2	Challenges in chemical reaction engineering education —	<b>235</b>
12.2.1	From Jan's recollection —	<b>235</b>
12.2.2	From René's recollection —	<b>238</b>
12.2.3	CRE as a language game linked to teaching —	<b>238</b>
12.3	Guidelines to use this book in academic education —	<b>239</b>
12.4	Guidelines to use this book in industry —	<b>240</b>
12.5	Education options for industry practitioners —	<b>240</b>
12.5.1	Learning course: industrial chemical reaction engineering and process concept design for nonchemical engineers —	<b>240</b>
12.5.2	Hands-on course: industrial reaction engineering and conceptual process design —	<b>241</b>
12.5.3	Course program —	<b>241</b>

12.6	Position of reaction engineering in chemical engineering curriculum —	<b>244</b>
12.7	Takeaway learning points —	<b>244</b>
	References —	<b>245</b>
<b>13</b>	<b>Industrial cases —</b>	<b>246</b>
13.1	Introduction —	<b>246</b>
13.2	Gas-to-liquid (GTL) Shell case —	<b>246</b>
13.2.1	Introduction to GTL case —	<b>246</b>
13.2.2	A consecutive or a parallel reaction? —	<b>247</b>
13.2.3	Flory-Schulz distributions —	<b>248</b>
13.2.4	Why Shell experts “like” fixed bed reactors for GTL? —	<b>250</b>
13.3	Ethyl benzene peroxidation reactor (EBHP) —	<b>254</b>
13.3.1	Introduction to the case —	<b>254</b>
13.3.2	Reaction description —	<b>255</b>
13.3.3	The liquid-phase RTD experiments —	<b>256</b>
13.3.4	Results of the liquid-phase RTD experiments —	<b>257</b>
13.3.5	Results of the gas phase RTD experiments —	<b>259</b>
13.3.6	Commercial plant improvements —	<b>263</b>
13.3.7	Takeaway learning points —	<b>264</b>
13.4	A new catalyst shape: pressure drop and packing density —	<b>265</b>
13.4.1	Introduction —	<b>265</b>
13.4.2	Initial evaluation —	<b>266</b>
13.4.3	Experimental results —	<b>267</b>
13.4.4	Takeaway learning points —	<b>267</b>
13.5	Heavy residue oil upgrading: reactor type selections and development —	<b>268</b>
13.5.1	Heavy residue upgrading introduction —	<b>268</b>
13.5.2	Heavy residue upgrading reaction chemistry —	<b>269</b>
13.5.3	Shell bunker flow selection and the development to commercial scale —	<b>270</b>
13.5.4	LC-FINING™ residue hydrocracking in three-phase slurry-ebullated-bed reactor —	<b>274</b>
13.5.5	Heavy oil upgrading by coking with Exxon Flexicoker fluid bed —	<b>275</b>
13.5.6	Reactor type comparison – heavy petroleum upgrade —	<b>275</b>
13.5.7	Exercises —	<b>276</b>
13.5.8	Takeaway learning points —	<b>276</b>
13.6	Reactor stability in an adiabatic trickle-bed reactor —	<b>277</b>
13.7	Three-phase slurry-reactive distillation —	<b>279</b>
13.7.1	Introduction —	<b>279</b>
13.7.2	Takeaway learning points —	<b>280</b>
13.8	Fluid bed retorting shale oil —	<b>280</b>



13.8.1	Project starting points —	280
13.8.2	Reaction kinetics, reactors, and process concept selections —	281
13.8.3	Shale characteristics —	282
13.8.4	Process concept —	282
13.8.5	Process conditions —	282
13.8.6	Process research items —	283
13.8.7	Takeaway learning points —	285
	References: fluid bed retorting of shale —	286
<b>14</b>	<b>Education case study: polyolefin CRE and scale-up —</b>	<b>287</b>
14.1	Introduction —	287
14.2	Discovery-stage reactor family selection —	287
14.3	Concept stage —	288
14.3.1	Scale-independent basics —	288
14.3.2	Chemistry and stoichiometry of the reaction —	288
14.3.3	Heat of reactions —	291
14.3.4	Physical properties —	292
14.3.5	Reaction engineering concept design —	292
14.3.6	Solid-phase residence time distribution —	293
14.3.7	Mass transfer limitations and concept design choices —	295
14.3.8	Heat transfer limitations and concept design —	297
14.3.9	Modeling for reactor sizing —	303
14.4	Feasibility stage —	304
14.4.1	Introduction —	304
14.4.2	Commercial-scale design in feasibility stage —	304
14.5	Development stage —	310
14.5.1	Pilot plant design —	310
14.5.2	Economics commercial scale, pilot plant and mock-up model —	313
14.5.3	Risks and value of information assessment —	313
14.5.4	Development: front-end engineering design —	315
14.6	Commercial-scale implementation (EPC and start-up) —	315
14.7	Exercises —	315
14.7.1	Exercise 1: Thiele modulus description and calculation for polyolefin catalyst —	315
14.7.2	Exercise 2: temperature catalyst particle —	316
14.7.3	Exercise 3: polyethylene reactor design —	316
14.8	Takeaway learning points —	316
14.9	List of symbols —	318
	References —	318