17

CHEMICAL REACTORS

In this chapter, the principles of chemical kinetics and catalysis are discussed. The basic rate equations are presented along with descriptions of operating modes and a wide variety of equipment that is suitable as chemical reactors. Few rules are generally applicable to the design of equipment for chemical reactions. The broad classes of reactors include stirred tanks, empty or packed beds in tubes, vessels and shell-and-tube devices, and highly specialized configurations in which heat transfer may be provided. Many design factors in individual cases are balanced to achieve economic optima. The general rules of other chapters for design of pressure vessels, heat exchangers, agitators, and so on, apply to chemical reactors.

The literature in this field is so abundant that only the most significant research that has resulted in commercialization is presented. The material reported is satisfactory for design purposes, although newer techniques are reported in the literature but may not be better than what is presented in this chapter.

There is a plethora of reactor designs, therefore, the most commonly used will be presented in this chapter. Examples of commercial reactors successfully employed in industry are presented but this is by no means to be construed as a comprehensive treatment. Due to space constraints, the editors had to make decisions concerning what was to be included in the chapter.

17.1. DESIGN BASIS AND SPACE VELOCITY

DESIGN BASIS

Although the intent of this chapter is not detailed design, it is in order to state what is included in a proper design basis, for example at least these items:

1. Stoichiometry of the participating reactions.
2. Thermal and other physical properties.
3. Heats of reaction and equilibrium data.
4. Rate of reaction, preferably in equation form, relating it to composition, temperature, pressure, impurities, catalysts and so on. Alternately tabular or graphical data relating compositions to time and the other variables listed.
5. Activity of the catalyst as a function of onstream time.
6. Mode of catalyst reactivation or replacement.
7. Stability and controllability of the process.
8. Special considerations of heat and mass transfer.
9. Corrosion and safety hazards.

REACTION TIMES

In practical cases reaction times vary from fractions of a second to many hours. The compilation of Table 17.1 of some commercial practices may be a basis for choosing by analogy an order of magnitude of reactor sizes for other processes.

For ease of evaluation and comparison, an apparent residence time often is used instead of the true one; it is defined as the ratio of the reactor volume to the inlet volumetric flow rate,

$$\bar{t}_{\text{app}} = V_r/V'_0$$

On the other hand, the true residence time, $\bar{t}$, must be found by integration,

$$\bar{t} = \int dV_r/V' = \int dn'_r/rV'.$$

Since the rate of reaction r and the volumetric flow rate V' at each position depend on T, P, and local molal flow rate n' of the key component of the reacting mixture, finding the true residence time is an involved process requiring many data. The easily evaluated apparent residence time usually is taken as adequate for rating sizes of reactors and for making comparisons.

A related concept is that of space velocity which is the ratio of a flow rate at STP (60°F, 1 atm usually) to the size of the reactor. The most common versions of space velocities in typical units are:

GHSV (gas hourly space velocity) = (volumes of feed as gas at STP/hr)/(volume of the reactor or its content of catalyst) = (SCFH gas feed)/cuft.

LHSV (liquid hoiurly space velocity) = (Volume of liquid feed at 60°F/hr)/volume of reactor or catalyst) = (SCFH liquid feed)/cuft.

WHSV (weight hourly space velocity) = (lb of feed/hr)/(lb of catalyst). Other combinations of units of the flow rate and reactor size often are used in practice, for instance.

BPSD/lb = (barrels of liquid feed at 60°F per stream day)/(lb catalyst), but it is advisable to write out such units in each case to avoid confusion with the standard meanings of the given acronyms. Since the apparent residence time is defined in terms of the actual inlet conditions rather than at standard T and P, it is not the reciprocal of GHSV or LHSV, although the units are the same.

17.2. RATE EQUATIONS AND OPERATING MODES

The equations of this section are summarized and extended in Table 17.2. The term "rate of reaction" used here is the rate of decomposition per unit volume,

$$r_a = -\frac{1}{V}\frac{dn_a}{dt}, \text{mol/(unit time)(unit volume)}. \tag{17.1}$$

A rate of formation will have the opposite sign. When the volume is constant, the rate is the derivative of the concentration

$$r_a = -\frac{dC_a}{dt}, \text{at constant volume}. \tag{17.2}$$

In homogeneous environments the rate is expressed by the law of mass action in terms of powers of the concentrations of the reacting substances

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = kC_a^{\alpha}C_b^{\beta}\cdots. \tag{17.3}$$

When the reaction mechanism truly follows the stoichiometric equation

TABLE 17.1. Residence Times and/or Space Velocities in Industrial Chemical Reactors

Product (raw materials)	Type	Reactor phase	Catalyst	Conditions		Residence time or space velocity	Source and page
				T, °C	*P*, atm		
1. Acetaldehyde (ethylene, air)	FB	L	Cu and Pd chlorides	50–100	8	6–40 min	[*2*] 1, [*7*] 3
2. Acetic anhydride (acetic acid)	TO	L	Triethyl phosphate	700–800	0.3	0.25–5 s	[*2*]
3. Acetone (*i*-propanol)	MT	LG	Ni	300	1	2.5 h	[*1*] *1* 314
4. Acrolein (formaldehyde, acetaldehyde)	FL	G	MnO, silica gel	280–320	1	0.6 s	[*1*] *1* 384, [*7*] 33
5. Acrylonitrile (air, propylene, ammonia)	FL	G	Bi phosphomolybdate	400	1	4.3 s	[*3*] 684, [*2*] 47
6. Adipic acid (nitration of cyclohexanol)	TO	L	Co naphthenate	125–160	4–20	2 h	[*2*] 51, [*7*] 49
7. Adiponitrile (adipic acid)	FB	G	H_3BO_3 H_3PO_4	370–410	1	3.5–5 s 350–500 GHSV	[*1*] *2* 152 [*7*] 52
8. Alkylate (*i*-C_4, butenes)	CST	L	H_2SO_4	5–10	2–3	5–40 min	[*4*] 223
9. Alkylate (*i*-C_4, butenes)	CST	L	HF	25–38	8–11	5–25 min	[*4*] 223
10. Allyl chloride (propylene, Cl_2)	TO	G	N.A.	500	3	0.3–1.5 s	[*1*] *2* 416, [*7*] 67
11. Ammonia (H_2, N_2)	FB	G	Fe	450	150	28 s 7,800 GHSV	[*6*] 61
12. Ammonia (H_2, N_2)	FB	G	Fe	450	225	33 s 10,000 GHSV	[*6*] 61
13. Ammonia oxidation	Flame	G	Pt gauze	900	8	0.0026 s	[*6*] 115
14. Aniline (nitrobenzene, H_2)	B	L	$FeCl_2$ in H_2O	95–100	1	8 h	[*1*] *3* 289
15. Aniline (nitrobenzene, H_2)	FB	G	Cu on silica	250–300	1	0.5–100 s	[*7*] 82
16. Aspirin (salicylic acid, acetic anhydride)	B	L	None	90	1	>1 h	[*7*] 89
17. Benzene (toluene)	TU	G	None	740	38	48 s 815 GHSV	[*6*] 36, [*9*] 109
18. Benzene (toluene)	TU	G	None	650	35	128 s	[*1*] *4* 183, [*7*] 98
19. Benzoic acid (toluene, air)	SCST	LG	None	125–175	9–13	0.2–2 h	[*7*] 101
20. Butadiene (butane)	FB	G	Cr_2O_3, Al_2O_3	750	1	0.1–1 s	[*7*] 118
21. Butadiene (1-butene)	FB	G	None	600	0.25	0.001 s 34,000 GHSV	[*3*] 572
22. Butadiene sulfone (butadiene, SO_2)	CST	L	*t*-butyl catechol	34	12	0.2 LHSV	[*1*] *5* 192
23. *i*-Butane (*n*-butane)	FB	L	$AlCl_3$ on bauxite	40–120	18–36	0.5–1 LHSV	[*4*] 239, [*7*] 683
24. *i*-Butane (*n*-butane)	FB	L	Ni	370–500	20–50	1–6 WHSV	[*4*] 239
25. Butanols (propylene hydroformylation)	FB	L	PH_3–modified Co carbonyls	150–200	1,000	100 g/L–h	[*1*] *5* 373
26. Butanols (propylene hydroformylation)	FB	L	Fe pentacarbonyl	110	10	1 h	[*7*] 125
27. Calcium stearate	B	L	None	180	5	1–2 h	[*7*] 135
28. Caprolactam (cyclohexane oxime)	CST	L	Polyphosphoric acid	80–110	1	0.25–2 h	[*1*] *6* 73, [*7*] 139
29. Carbon disulfide (methane, sulfur)	Furn.	G	None	500–700	1	1.0 s	[*1*] *6* 322, [*7*] 144
30. Carbon monoxide oxidation (shift)	TU	G	Cu-Zn or Fe_2O_3	390–220	26	4.5 s 7,000 GHSV	[*6*] 44
30′. Port. cement	Kiln	S		1400–1700	1	10 h	[*11*]
31. Chloral (Cl_2, acetaldehyde)	CST	LG	None	20–90	1	140 h	[*7*] 158
32. Chlorobenzenes (benzene, Cl_2)	SCST	LG	Fe	40	1	24 h	[*1*] *8* 122
33. Coking, delayed (heater)	TU	LG	None	490–500	15–4	250 s	[*1*] *10* 8
34. Coking, delayed (drum, 100 ft max.)	B	LG	None	500–440	4	0.3–0.5 ft/s vapor	[*1*] *10* 8
35. Cracking, fluid-catalytic	FL	G	SiO_2, Al_2O_3	470–540	2–3	0.5–3 WHSV	[*4*] 162
36. Cracking, hydro-(gas oils)	FB	LG	Ni, SiO_2, Al_2O_3	350–420	100–150	1–2 LHSV	[11]
37. Cracking (visbreaking residual oils)	TU	LG	None	470–495	10–30	450 s 8 LHSV	[*11*]
38. Cumene (benzene, propylene)	FB	G	H_3PO_4	260	35	23 LHSV	[*11*]

TABLE 17.1.—(*continued*)

Product (raw materials)	Type	Reactor phase	Catalyst	Conditions		Residence time or space velocity	Source and page
				T, °C	*P*, atm		
39. Cumene hydroperoxide (cumene, air)	CST	L	Metal porphyrins	95–120	2–15	1–3 h	[*7*] 191
40. Cyclohexane (benzene, H_2)	FB	G	Ni on Al_2O_3	150–250	25–55	0.75–2 LHSV	[*7*] 201
41. Cyclohexanol (cyclohexane, air)	SCST	LG	None	185–200	48	2–10 min	[*7*] 203
42. Cyclohexanone (cyclohexanol)	CST	L	N.A.	107	1	0.75 h	[*8*] (1963)
43. Cyclohexanone (cyclohexanol)	MT	G	Cu on pumice	250–350	1	4–12 s	[*8*] (1963)
44. Cyclopentadiene (dicyclopentadiene)	TU	G	None	220–300	1–2	0.1–0.5 LHSV	[*7*] 212
45. DDT (chloral, chlorobenzene)	B	L	Oleum	0–15	1	8 h	[*7*] 233
46. Dextrose (starch)	CST	L	H_2SO_4	165	1	20 min	[*8*] (1951)
47. Dextrose (starch)	CST	L	Enzyme	60	1	100 min	[*7*] 217
48. Dibutylphthalate (phthalic anhydride, butanol)	B	L	H_2SO_4	150–200	1	1–3 h	[*7*] 227
49. Diethylketone (ethylene, CO)	TO	L	Co oleate	150–300	200–500	0.1–10 h	[*7*] 243
50. Dimethylsulfide (methanol, CS_2)	FB	G	Al_2O_3	375–535	5	150 GHSV	[*7*] 266
51. Diphenyl (benzene)	MT	G	None	730	2	0.6 s 3.3 LHSV	[*7*] 275, [*8*] (1938)
52. Dodecylbenzene (benzene, propylene tetramer)	CST	L	$AlCl_3$	15–20	1	1–30 min	[*7*] 283
53. Ethanol (ethylene, H_2O)	FB	G	H_3PO_4	300	82	1,800 GHSV	[*2*] 356, [*7*] 297
54. Ethyl acetate (ethanol, acetic acid)	TU, CST	L	H_2SO_4	100	1	0.5–0.8 LHSV	[*10*] 45, 52, 58
55. Ethyl chloride (ethylene, HCl)	TO	G	$ZnCl_2$	150–250	6–20	2 s	[*7*] 305
56. Ethylene (ethane)	TU	G	None	860	2	1.03 s 1,880 GHSV	[*3*] 411, [*6*] 13
57. Ethylene (naphtha)	TU	G	None	550–750	2–7	0.5–3 s	[*7*] 254
58. Ethylene, propylene chlorohydrins (Cl_2, H_2O)	CST	LG	None	30–40	3–10	0.5–5 min	[*7*] 310, 580
59. Ethylene glycol (ethylene oxide, H_2O)	TO	LG	1% H_2SO_4	50–70	1	30 min	[*2*] 398
60. Ethylene glycol (ethylene oxide, H_2O)	TO	LG	None	195	13	1 h	[*2*] 398
61. Ethylene oxide (ethylene, air)	FL	G	Ag	270–290	1	1 s	[*2*] 409, [*7*] 322
62. Ethyl ether (ethanol)	FB	G	WO_3	120–375	2–100	30 min	[*7*] 326
63. Fatty alcohols (coconut oil)	B	L	Na, solvent	142	1	2 h	[*8*] (1953)
64. Formaldehyde (methanol, air)	FB	G	Ag gauze	450–600	1	0.01 s	[*2*] 423
65. Glycerol (allyl alcohol, H_2O_2)	CST	L	H_2WO_4	40–60	1	3 h	[*7*] 347
66. Hydrogen (methane, steam)	MT	G	Ni	790	13	5.4 s 3,000 GHSV	[*6*] 133
67. Hydrodesulfurization of naphtha	TO	LG	Co-Mo	315–500	20–70	1.5–8 LHSV 125 WHSV	[*4*] 285, [*6*] 179, [*9*] 201
68. Hydrogenation of cottonseed oil	SCST	LG	Ni	130	5	6 h	[*6*] 161
69. Isoprene (*i*-butene, formaldehyde)	FB	G	HCl, silica gel	250–350	1	1 h	[*7*] 389
70. Maleic anhydride (butenes, air)	FL	G	V_2O_5	300–450	2–10	0.1–5 s	[*7*] 406
71. Melamine (urea)	B	L	None	340–400	40–150	5–60 min	[*7*] 410
72. Methanol (CO, H_2)	FB	G	ZnO, Cr_2O_3	350–400	340	5,000 GHSV	[*7*] 421
73. Methanol (CO, H_2)	FB	G	ZnO, Cr_2O_3	350–400	254	28,000 GHSV	[*3*] 562
74. *o*-Methyl benzoic acid (xylene, air)	CST	L	None	160	14	0.32 h 3.1 LHSV	[*3*] 732
75. Methyl chloride (methanol, Cl_2)	FB	G	Al_2O_3 gel	340–350	1	275 GHSV	[*2*] 533
76. Methyl ethyl ketone (*2*-butanol)	FB	G	ZnO	425–475	2–4	0.5–10 min	[*7*] 437
77. Methyl ethyl ketone (*2*-butanol)	FB	G	Brass spheres	450	5	2.1 s 13 LHSV	[*10*] 284
78. Nitrobenzene (benzene, HNO_3)	CST	L	H_2SO_4	45–95	1	3–40 min	[*7*] 468
79. Nitromethane (methane, HNO_3)	TO	G	None	450–700	5–40	0.07–0.35 s	[*7*] 474
80. Nylon-6 (caprolactam)	TU	L	Na	260	1	12 h	[*7*] 480
81. Phenol (cumene hydroperoxide)	CST	L	SO_2	45–65	2–3	15 min	[*7*] 520
82. Phenol (chlorobenzene, steam)	FB	G	Cu, Ca phosphate	430–450	1–2	2 WHSV	[*7*] 522
83. Phosgene (CO, Cl_2)	MT	G	Activated carbon	50	5–10	16 s 900 GHSV	[*11*]
84. Phthalic anhydride (*o*-xylene, air)	MT	G	V_2O_5	350	1	1.5 s	[*3*] 482, 539, [*7*] 529
85. Phthalic anhydride (naphthalene, air)	FL	G	V_2O_5	350	1	5 s	[*9*] 136, [*10*] 335

(*continued*)

TABLE 17.1.—(*continued*)

Product (raw materials)	Type	Reactor phase	Catalyst	Conditions		Residence time or space velocity	Source and page
				T, °C	*P*, atm		
86. Polycarbonate resin (bisphenol-A, phosgene)	B	L	Benzyltri-ethylammonium chloride	30–40	1	0.25–4 h	[*7*] 452
87. Polyethylene	TU	L	Organic peroxides	180–200	1,000–1,700	0.5–50 min	[*7*] 547
88. Polyethylene	TU	L	Cr_2O_3, Al_2O_3, SiO_2	70–200	20–50	0.1–1,000 s	[*7*] 549
89. Polypropylene	TO	L	R_2AlCl, $TiCl_4$	15–65	10–20	15–100 min	[*7*] 559
90. Polyvinyl chloride	B	L	Organic peroxides	60	10	5.3–10 h	[*6*] 139
91. *i*-Propanol (propylene, H_2O)	TO	L	H_2SO_4	70–110	2–14	0.5–4 h	[*7*] 393
92. Propionitrile (propylene, NH_3)	TU	G	CoO	350–425	70–200	0.3–2 LHSV	[*7*] 578
93. Reforming of naphtha (H_2/hydrocarbon = 6)	FB	G	Pt	490	30–35	3 LHSV 8,000 GHSV	[*6*] 99
94. Starch (corn, H_2O)	B	L	SO_2	25–60	1	18–72 h	[*7*] 607
95. Styrene (ethylbenzene)	MT	G	Metal oxides	600–650	1	0.2 s 7,500 GHSV	[*5*] 424
96. Sulfur dioxide oxidation	FB	G	V_2O_5	475	1	2.4 s 700 GHSV	[*6*] 86
97. *t*-Butyl methacrylate (methacrylic acid, *i*-butane)	CST	L	H_2SO_4	25	3	0.3 LHSV	[*1*] *5* 328
98. Thiophene (butane, S)	TU	G	None	600–700	1	0.01–1 s	[*7*] 652
99. Toluene diisocyanate (toluene diamine, phosgene)	B	LG	None	200–210	1	7 h	[*7*] 657
100. Toluene diamine (dinitrotoluene, H_2)	B	LG	Pd	80	6	10 h	[*7*] 656
101. Tricresyl phosphate (cresyl, $POCl_3$)	TO	L	$MgCl_2$	150–300	1	0.5–2.5 h	[*2*] 850, [*7*] 673
102. Vinyl chloride (ethylene, Cl_2)	FL	G	None	450–550	2–10	0.5–5 s	[*7*] 699

Abbreviations

Reactors: batch (B), continuous stirred tank (CST), fixed bed of catalyst (FB), fluidized bed catalyst (FL), furnace (Furn.), multitubular (MT), semicontinuous stirred tank (SCST), tower (TO), tubular (TU).

Phases: liquid (L), gas (G), both (LG).

Space velocities (hourly): gas (GHSV), liquid (LHSV), weight (WHSV).

Not available (N.A.)

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$$v_aA + v_bB + \cdots \rightarrow \text{products}, \tag{17.4}$$

the exponents are the stoichiometric coefficients; thus,

$$r_a = k(C_a)v_a(C_b)v_b\cdots, \tag{17.5}$$

but α, β, … often are purely empirical values—integral or nonintegral, sometimes even negative.

The coefficient k is called the specific rate coefficient. It is taken to be independent of the concentrations of the reactants but does depend primarily on temperature and the nature and concentration of catalysts. Temperature dependence usually is represented by

$$k = k_\infty \exp(-E/RT) = \exp(a' - b'/T), \tag{17.6}$$

where E is the energy of activation.

Specific rates of reactions of practical interest cannot be found by theoretical methods of calculation nor from correlations in terms of the properties of the reactants. They must be found empirically in every case together with the complete dependence of the rate of reaction on concentrations, temperature, and other pertinent factors. The analysis of experimental data will be ignored here since the emphasis is placed on the use of known rate equations.

Integration of the rate equation is performed to relate the composition to the reaction time and the size of the equipment. From a rate equation such as

$$-\frac{dC_a}{dt} = kC_a^\alpha C_b^\beta C_c^\gamma, \tag{17.7}$$

TABLE 17.2. Basic Rate Equations

1. The reference reaction is

$$v_aA + v_bB + \cdots \rightarrow v_rR + v_SS + \cdots$$
$$\Delta v = v_r + v_s + \cdots - (v_a + v_b + \cdots)$$

2. Stoichiometric balance for any component i,

$$n_i = n_{i0} \pm (v_i/v_a)(n_{a0} - n_a)$$
$$\begin{cases} + & \text{for product (right-hand side, RHS)} \\ - & \text{for reactant (left-hand side, LHS)} \end{cases}$$
$$C_i = C_{i0} \pm (V_i/V_a)(C_{a0} - C_a), \text{ at constant } T \text{ and } V \text{ only}$$
$$n_t = n_{to} + (\Delta v/v_a)(n_{a0} - n_a)$$

3. Law of mass action

$$r_a = -\frac{1}{V_r}\frac{dn_a}{dt} = kC_a^{V_\partial}C_b^{V_b}\cdots$$
$$= kC_a^{V_a}[C_{b0} - (v_b/v_a)(C_{a0} - C_a)]^{V_b}\cdots$$
$$r_a = kC_a^{\alpha}[C_{b0} - (v_b/v_a)(C_{a0} - C_a)]^{\beta}\cdots$$

where it is not necessarily true that $\alpha = v_{a'}\beta = v_{b'}\cdots$

4. At constant volume, $C_a = n_a/V_r$

$$kt = \int_{ca}^{C_{a0}} \frac{1}{C_a^{\alpha}[C_{b0} - (v_b/v_a)(C_{a0} - C_a)^{\beta}\cdots} dC_a$$
$$kt = \int_{na}^{n_{a0}} \frac{V_{\cdots}^{-1+\alpha+\beta}}{n_a^{\alpha}[n_{b0} - (v_b/v_a)(n_{a0} - n_a)]^{\beta}\cdots} dn_a$$

Completed integrals for some values of α and β are in Table 17.3

5. Ideal gases at constant pressure:

$$V_r = \frac{n_tRT}{P} = \frac{RT}{P}\left[n_{r0} + \frac{\Delta v}{V_a}(n_{a0} - n_a)\right]$$
$$r_a = kC_a^{\alpha}$$
$$kt = \left(\frac{RT}{P}\right)^{\alpha-1}\int_{n_a}^{n_{a0}} \frac{[n_{t0} + (\Delta v/v_a)(n_{a0} - n_a)]^{\alpha-1}}{n_a^{\alpha}} dn_a$$

6. Temperature effect} on the specific rate:

$$k = k_\infty \exp(-E/RT) = \exp(a' - b'/T)$$
$$E = \text{energy of activation}$$

7. Simultaneous reactions: The overall rate is the algebraic sum of the rates of the individual reaction For example, take the three reaction:

   1. $A + B \xrightarrow{k_1} C + D.$
   2. $C + D \xrightarrow{k_1} A + B.$
   3. $A + C \xrightarrow{k_1} E.$

   The rates are related by:

$$r_a = r_{a1} + r_{a2} + r_{a3} = k_1C_aC_b - k_2C_cC_d + k_3C_aC_c$$
$$r_b = -r_d = k_1C_aC_b - k_2C_cC_d$$
$$r_c = -k_1C_aC_b + k_2C_cC_d + k_3C_aC_c$$
$$r_e = -k_3C_aC_c$$

The number of independent rate equations is the same as the number of independent stoichiometric relations. In the present example, reaction 1 and 2 are a reversible reaction and are not independent. Accordingly, C_c and C_d, for example, can be eliminated from the equations for r_a and r_a which then become an integrable system. Usually only systems of linear differential equations with constant coefficients are solvable analytically. Many such cases are treated by Rodiguin and Rodiguina (1964).

8. Mass transfer resistance:

$$C_{ai} = \text{interfacial concentration of reactant A}$$
$$r_a = -\frac{dC_a}{dt} = k_d(C_a - C_{ai}) = kC_{ai}^{\alpha} = k\left(C_a - \frac{r_a}{k_d}\right)^{\alpha}$$
$$kt = \int_{C_a}^{C_{a0}} \frac{1}{(C_a - r_a/k_d)^{\alpha}} dC_a$$

The relation between r_a and C_a must be established (numerically if need be) from the second line before the integration can be completed

9. Solid-catalyzed reaction, some Langmuir-Hinshelwood mechanisms for The reference reaction A + B → R + S.
   1. Adsorption rate of A controlling

$$r_a = -\frac{1}{V}\frac{dn_a}{dt} = kP_a\theta_V$$
$$\theta_V = 1/\left[1 + \frac{K_aP_rP_s}{K_eP_b} + K_bP_b + K_rP_r + K_sP_s + K_I, P_I,\right]$$
$$K_e = P_rP_s/P_aP_b \text{ (equilibrium constant)}$$

   / is an adsorbed balance that is chemically inert

   2. Surface reaction rate controlling:

$$r = kP_aP_b\theta_V^2$$
$$\theta_V = 1\Big/\left(1 + \sum K_jP_j\right),$$

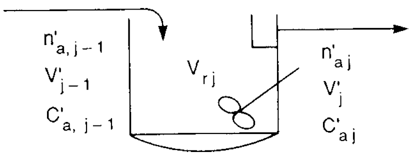
   summation over all substances absorbed

   3. Reaction $A_2 + B \rightarrow R + S$, with A_2 dissociated upon adsorption and with surface reaction rate controlling:

$$r_a = kP_aP_b\theta_V^3$$
$$\theta_V = 1/(1 + \sqrt{K_aP_a} + K_bP_b + \cdots)$$

   4. At constant P and T the P_i are eliminated in favor of n_i and the total pressure by

$$P_a = \frac{n_a}{n_t}P$$
$$P_i = \frac{n_i}{n_t}P = \frac{n_{i0} \pm (v_i/v_a)(n_{a0} - n_a)}{n_{to} + (\Delta v/v_a)(n_{a0} - n_a)}P$$
$$\begin{cases} + & \text{for products, RHS} \\ - & \text{for reactants, LHS} \end{cases}$$
$$V = \frac{n_tRT}{P}$$
$$kt = \int_{n_a}^{n_{a0}} \frac{1}{VP_aP_b\theta_V^2}, \text{ for a case (2) batch reaction}$$



(*continued*)

TABLE 17.2.—(*continued*)

10. A continuous stirred tank reactor battery (CSTR) Material balances:

$$n'_{a0} = n'_a + r_{a1} V_{r1}$$
$$\vdots$$
$$n'_{a,j-1} = n'_{aj} + r_{aj} V_{rj}, \text{for the } j\text{th stage}$$

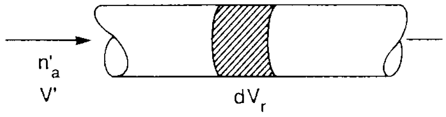
For a first order reaction, with $r_a = kC_{a'}$

$$\frac{C_{aj}}{C_{a0}} = \frac{1}{(1+k_1\bar{t}_1)(1+k_2\bar{t}_2)\cdots(1+k_j\bar{t}_j)} = \frac{1}{(1+k\bar{t}_i)^j},$$

for j tanks in series with the same temperatures and residence times $\bar{t}_i = V_{ri}/V'_i$, where V' is the volumetric flow rate

11. Plug flow reactor (PFR):

$$\begin{aligned} r_a &= -\frac{dn'_a}{dV_r} = kC_a^\alpha C_b^\beta \cdots \\ &= k(n'_a/V')^\alpha (n'_b/V')^\beta \cdots \end{aligned}$$



12. Material and energy balances for batch, CSTR and PFR are in Tables 17.4, 17.5, and 17.6

13. Notation

A, B, R, S are participants in the reaction; the letters also are used to represent concentrations

$C_i = n_i/V_r$ or n'_i/V', concentration
n_i = mols of component i in the reactor
n_i = molal flow rate of component i
V_r = volume of reactor
V' = volumetric flow rate
v_i = stoichiometric coefficient
r_i = rate of reaction of substance i [mol/(unit time)(unit volume)]
α, β = empirical exponents in a rate equation

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the concentrations C_b and C_c first must be eliminated with the aid of the stoichiometric equation of the process. Item 4 of Table 17.2 is an example. When several reactions occur simultaneously, the overall rate of a particular participant is the algebraic sum of its rates in individual reactions. Item 7 of Table 17.2 is an example. The number of differential equations representing the reacting system is the same as the number of independent stoichiometric equations; appropriate concentrations are eliminated with stoichiometry to develop an integrable set of equations. Integrals of common isothermal, constant volume rate equations are summarized in Table 17.3, and a simple case of a process at constant pressure is item 5 of Table 17.3.

An overall conversion rate may depend on rates of mass transfer between phases as well as chemical rates. In the simplest case, mass transfer and chemical transformation occur in series; advantage is taken of the equality of these two rates at steady state conditions to eliminate interfacial concentrations from the rate equations and thus to permit integration. Item 8 of Table 17.2 is an example.

Rates of fluid phase reactions catalyzed by solids also can be represented at least approximately by powers of the concentrations. A more fundamental approach, however, takes into account mechanisms of adsorption and of reaction on the catalyst surface. A few examples of resulting equations are in item 9 of Table 17.2.

Practical solid-catalyzed rate processes also may be influenced by rates of diffusion to the external and internal surfaces. In the latter case, the rate equation is modified by inclusion of a catalyst effectiveness to become

$$r_a = k\eta f(C_a). \tag{17.8}$$

The effectiveness, η, is a measure of the utilization of the internal surface of the catalyst and C_a is the concentration of the reactant, a, at the external catalyst surface. It depends on the dimensions of the catalyst particle and its pores, on the diffusivity, specific rate, and heat of reaction. With a given kind of catalyst, the only control is particle size to which the effectiveness is proportional; a compromise must be made between effectiveness and pressure drop. In simple cases η can be related mathematically to its parameters, but in such important practical cases as ammonia synthesis its dependence on parameters is complex and strictly empirical. Section 17.5 deals with this topic.

Reaction processes may be conducted under nonflow or steady flow conditions. One mode of the latter is tubular flow or, in the limiting case, plug flow, in which all molecules have substantially the same residence time. The rate equation for a plug flow reactor (PFR) is

$$r_a = -\frac{dn'_a}{dV_r} = kC_a^\alpha C_b^\beta \cdots = k\left(\frac{n'_a}{V'}\right)^\alpha \left(\frac{n'_b}{V'}\right)^\beta \cdots, \tag{17.9}$$

where V_r is the reactor volume and the primes (′) designate flow rates. Flow reactions of gases take place at substantially constant pressure so that V' will depend on the extent of conversion if there is a change in the number of mols. Item 11 of Table 17.2 is an example of the rate equation for such conditions.

The other mode of flow reaction employs one or more stirred tanks in series, which is called a continuous stirred tank (CSTR) battery. The rate of reaction in a single tank is

$$r_a = \frac{n'_{a0} - n'_a}{V_r} \simeq \frac{C_{a0} - C_a}{V_r/V'} = C_{a0} - C_a/\bar{t} = kC_a^\alpha C_b^\beta \cdots, \tag{17.10}$$

The relation in terms of concentrations is valid if the volumetric rates into and out of the tank are substantially the same. Stirring is assumed sufficient to maintain uniform composition and temperature in the tank; then the effluent conditions are the same as those of the tank. Relations for several tanks in series are in item 10 of Table 17.2.

17.3. MATERIAL AND ENERGY BALANCES OF REACTIONS

All chemical reactions are accompanied by some heat effects so that the temperature will tend to change, a serious result in view of the sensitivity of most reaction rates to temperature. Factors of equipment size, controllability, and possibly unfavorable product distribution of complex reactions often necessitate provision of means of heat transfer to keep the temperature within bounds. In practical operation of nonflow or tubular flow reactors, truly isothermal conditions are not feasible even if they were desirable. Individual continuous stirred tanks, however, do maintain substantially uniform temperatures at steady state when the mixing is intense

TABLE 17.3. Some Isothermal Rate Equations and Their Integrals

1. $A \rightarrow$ products:

$$-\frac{dA}{dt} = kA$$

$$\frac{A}{A_0} = \begin{cases} \exp[-k(t-t_0)], & \alpha = 1 \\ \left[\dfrac{1}{1+kA_0^{\alpha-1}(t-t0)}\right]^{1/(\alpha-1)}, & \alpha \neq 1 \end{cases}$$

2. $A + B \rightarrow$ products:

$$-\frac{dA}{dt} = kAB = kA(A+B_0-A_0)$$

$$k(t-t_0) = \frac{1}{B_0-A_0}\ln\frac{A_0(A+B_0-A_0)}{AB_0}$$

3. Reversible reaction $A \underset{k_3}{\overset{k_1}{\rightleftharpoons}} B$:

$$-\frac{dA}{dt} = k_1A - k_2(A_0+B_0-A) = (k_1+k_2)A - k_2(A_0+B_0)$$

$$(k_1+k_2)(t-t_0) = \ln\frac{k_1A_0-k_2B_0}{(k_1+k_2)A-k_2(A_0+B_0)}$$

4. Reversible reaction, second order, $A+B \underset{k_3}{\overset{k_1}{\rightleftharpoons}} R+S$

$$-\frac{dA}{dt} = k_1AB - k_2RS = k_1A(A+B_0-A_0) - k_2(A_0+R_0-A)(A_0+S_0-A)$$

$$= \alpha A^2 + \beta A - \gamma$$

$$\alpha = k_1 - k_2$$

$$\beta = k_1(B_0-A_0) + k_2(2A_0+R_0+S_0)$$

$$\gamma = k_2(A_0+R_0)(A_0+S_0)$$

$$q = \sqrt{\beta^2+4\alpha\gamma}$$

$$k(t-t_0) = \begin{cases} \dfrac{2\alpha A_0+\beta}{2\alpha A+\beta'} & q = 0 \\ \dfrac{1}{q}\ln\left[\left(\dfrac{2\alpha A_0+\beta-q}{2\alpha A_0+\beta+q}\right)\left(\dfrac{2\alpha A+\beta+q}{2\alpha A+\beta-q}\right)\right], & q \neq 0 \end{cases}$$

5. The reaction $v_aA+v_bB \rightarrow v_rR+v_sS$ between ideal gases at constant T and P

$$-\frac{dn_a}{dt}\ \frac{kn_a^{\alpha}}{V^{\alpha-1}}$$

$$V = n_t\frac{RT}{P} = \left[n_{t0} + \frac{\Delta v}{V_a}(n_{a0}-n_a)\right]\frac{RT}{P}$$

$$k(t-t_0) = \begin{cases} \displaystyle\int_{n_a}^{n_{a0}} \frac{V^{\alpha-1}}{n_a^{\alpha}} dn_{a'} \text{ in general} \\ \dfrac{RT}{P}\left[n_{b0} + \dfrac{\Delta v}{v_a}\left(\dfrac{l}{n_a} - \dfrac{1}{n_{a0}}\right) - \dfrac{\Delta v}{v_a}\ln\left(\dfrac{n_{a0}}{n_a}\right)\right], \text{when } \alpha = 2 \end{cases}$$

6. Equations readily solvable by Laplace transforms. For example:

$$A \underset{k_3}{\overset{k_1}{\rightleftharpoons}} B \overset{k_2}{\rightarrow} C$$

Rate equations are

$$-\frac{dA}{dt} = k_1A - k_2B$$

$$-\frac{dB}{dt} = -k_1A + (k_2+k_3)B$$

$$-\frac{dC}{dt} = -k_2B$$

Laplace transformations are made and rearranged to

$$(s+k_1)\overline{A} + k_3\overline{B} = A_0$$

$$-k_1\overline{A} + (s+k_2+k_3)\overline{B} = B_0$$

$$-k_2\overline{B} + s\overline{C} = C_0$$

These linear equations are solved for the transforms as

$$D = s^2 + (k_1+k_2+k_3)s + k_1k_2$$

$$\overline{A} = [A_0s + (k_2+k_3)A_0 + k_3B_0]/D$$

$$\overline{B} = [B_0s + k_1(A_0+B_0)]/D$$

$$\overline{C} = (k_2\overline{B} + C_0)/s$$

Inversion of the transforms can be made to find the concentrations A, B, and C as functions of the time t. Many such examples are solved by Rodiguin and Rodiguina (1964).

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enough; the level is determined by the heat of reaction as well as the rate of heat transfer provided.

In many instances the heat transfer aspect of a reactor is paramount. Many different modes have been and are being employed, a few of which are illustrated in Section 17.6. The design of such equipment is based on material and energy balances that incorporate rates and heats of reaction together with heat transfer coefficients. Solution of these balances relates the time, composition, temperature, and rate of heat transfer. Such balances are presented in Tables 17.4–17.7 for four processes:

1. Nonflow reactors.
2. Continuous stirred tanks.
3. Plug flow reactors.
4. Flow reactor packed with solid catalyst.

The data needed are the rate equation, energy of activation, heat of reaction, densities, heat capacities, thermal conductivity, diffusivity, heat transfer coefficients, and usually the stoichiometry of the process. Simplified numerical examples are given for some of these cases. Item 4 requires the solution of a system of partial differential equations that cannot be made understandable in concise form, but some suggestions as to the procedure are made.

17.4. NONIDEAL FLOW PATTERNS

The CSTR with complete mixing and the PFR with no axial mixing are limiting behaviors that can be only approached in practice. Residence time distributions in real reactors can be found with tracer tests.

RESIDENCE TIME DISTRIBUTION (RTD)

In the most useful form the test consists of a momentary injection of a known amount of inert tracer at the inlet of the operating vessel and monitoring of its concentration at the outlet. The data are used most conveniently in reduced form, as $E = C/\overline{C}_0$ in terms of $t_r = t/\bar{t}$, where

C = concentration of tracer at the outlet,
$\overline{C}_0$ = initial average concentration of tracer in the vessel,
$\bar{t} = V_r/V'$ = average residence time.

The plotted data usually are somewhat skewed bell-shapes. Some actual data are shown in Figure 17.1 together with lines for ideal CSTR and PFR. Such shapes often are represented

TABLE 17.4. Material and Energy Balances of a Nonflow Reaction

Rate equations:

$$r_a = -\frac{1}{V_r}\frac{dn_a}{d\theta} = kC_a^\alpha = k\left(\frac{n_a}{V_r}\right)^\alpha \tag{1}$$

$$k = \exp(a' - b'/T) \tag{2}$$

Heat of reaction:

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p dT \tag{3}$$

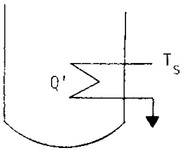
Rate of heat transfer:

$$Q' = UA(T_s - T) \tag{4}$$

(the simplest case is when UA and T_s are constant)
Enthalpy balance:

$$\frac{dT}{dn_a} = \frac{1}{\rho V_r \overline{C}_p}\left[\Delta H_r + \frac{UA(T_s - T)}{V_r k(n_a/V_r)}\right] \tag{5}$$

$$\frac{dT}{dC_a} = \frac{1}{\rho \overline{C}_p}\left[\Delta H_r + \frac{UA(T_s - T)}{V_r kC_a}\right] \tag{6}$$



$$T = T_0 \text{ when } C_a = C_{a0} \tag{7}$$

$$\overline{C}p = \frac{1}{\rho V_r}\sum n_i C_{pi} \tag{8}$$

Solve Eq. (6) to find $T = f(C_a)$; combine Eqs. (1) and (2) and integrate as

$$\theta = \int_{C_a}^{C_{a0}} \frac{1}{C_a^\alpha \exp[a' - b'/f(C_a)]} dC_a \tag{9}$$

Temperature and time as a function of composition are shown for two values of UA/V_r for a particular case represented by

$$\frac{dT}{dC_a} = \frac{1}{50}\left[5000 + 5T + \frac{UA(300 - T)}{V_r kC_a^2}\right]$$

$$k = \exp(16 - 5000/T)$$

$$T_0 = 350$$

$$C_{a0} = 1$$

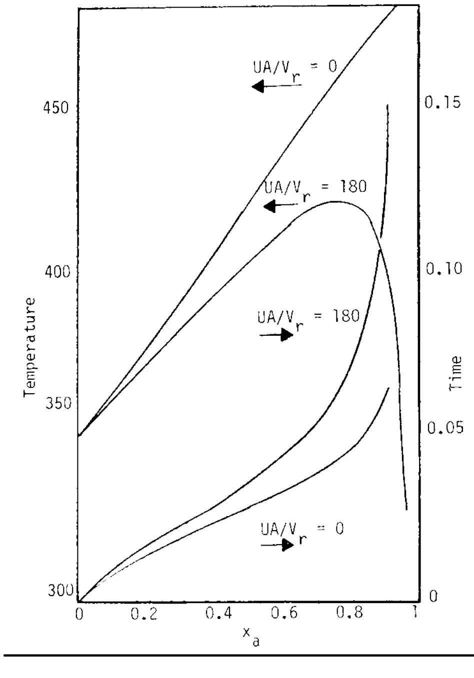


TABLE 17.5. Material and Energy Balance of a CSTR

The sketch identifies the nomenclature
Mean residence time:

$$t = V_r/V' \tag{1}$$

Temperature dependence:

$$k = \exp(a' - b'/T) \tag{2}$$

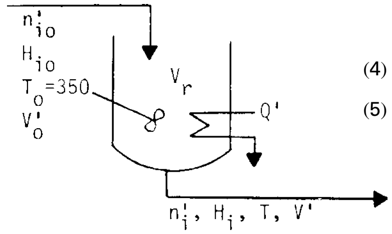
Rate equation:

$$r_a = kC_a^\alpha = kC_{a0}^\alpha(1 - x)^\alpha,\ x = (C_{a0} - C_a)/C_{a0} \tag{3}$$

Material balance:

$$C_{a0} = Ca + k\bar{t}C_a \tag{4}$$

$$x = k\bar{t}C_{a0}^{\alpha-1}(1 - x)^\alpha \tag{5}$$



Enthalpy balance:

$$\sum n'_i H_i - \sum n'_{io} H_{i0} = Q' - \Delta H_r(n'_{a0} - n'_a) \tag{6}$$

$$H_i = \int_{298}^{T} C_{pi} dT \tag{7}$$

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p dT \tag{8}$$

For the reaction $aA + bB \rightarrow rR + sS$,

$$\Delta C_p = rC_{pr} + sC_{ps} - aC_{pa} - bC_{pb} \tag{9}$$

When the heat capacities are equal and constant, the heat balance is

$$\overline{C}_p \rho V'(T - T_0) = Q' - \Delta H_{r298} V'(C_{a0} - C_a) \tag{10}$$

Example:

$k = \exp(16 - 5500/T)$
$C_{a0} = 5$ g mol/L
$V' = 2000$L/hr
$\Delta H_r = -5$ kcal/g mol
$\rho C_p = 0.9$ kcal/(L)(K)
$\alpha = 2$
$T_0 = 350$

	x = 0.90		x = 0.95	
$\bar{t}$	T	Q'	T	Q'
1	419.5	80	471.3	171
2	398.5	42	444.9	123
3	387.1	22	430.8	98
4	379.4	8	421.3	81
5	373.7	−2	414.2	68
6	369.1	−11	408.6	58
7	365.3	−17	404.0	50
8	362.1	−23	400.0	43
9	359.3	−28	396.6	36
10	356.9	−33	393.6	31

Eqs. (2) and (5) combine to

$$T = \frac{5500}{16 - \ln[x/5\bar{t}(1 - x)^2]}$$

and Eq. (10) becomes

$$Q' = 2[0.9(T - 350) - 25x], \text{ Mcal/hr}$$

The temperature and the rate of heat input Q' are tabulated as functions of the residence time for conversions of 90 and 95%

TABLE 17.6. Material and Energy Balances of a Plug Flow Reactor (PFR)

The balances are made over a differential volume dV_r of the reactor
Rate equation:

$$dV_r = \frac{-dn_a'}{r_a} \tag{1}$$

$$= -\frac{1}{k}\left(\frac{V'}{n_a}\right)^{\alpha} dn_a' \tag{2}$$

$$= -\exp\left(\frac{-a'+b'}{T}\right)\left(\frac{n'_t RT}{Pn_a'}\right)^{\alpha} dn_a' \tag{3}$$

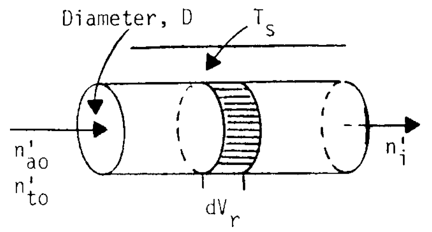
Enthalpy balance:

$$\Delta H_r = \Delta H_{r298} + \int_{298}^{T} \Delta C_p dT \tag{4}$$

$$\begin{aligned} dQ &= U(T_s - T)dA_p = \frac{4U}{D}(T_s - T)dV_r \\ &= -\frac{4U(T_s - T)}{Dr_a} dn_a' \end{aligned} \tag{5}$$

$$dQ + \Delta H_r dn_a' = \sum n_i dH_i = \sum n_i C_{pi} dT \tag{6}$$

$$\frac{dT}{dn_a'} = \frac{\Delta H_r - 4U(T_s - T)/Dr_a}{\sum n_i c_{\rho i}} = f(T, T_{s'} n_a') \tag{7}$$



At constant T_s, Eq. (7) may be integrated numerically to yield the temperature as a function of the number of mols

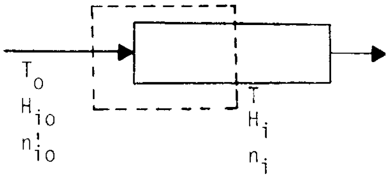
$$T = \phi(n_a') \tag{8}$$

Then the reactor volume is found by integration

$$V_r = \int_{n_a'}^{n'_{a0}} \frac{1}{\exp[a' - b'/\phi(n_a')][Pn_a'/n_{'t}R\phi(n_a')]^{\alpha}} dn_a' \tag{9}$$

Adiabatic process:

$$dQ = 0$$



The balance around one end of the reactor is

$$\sum n_{i0} H_{i0} - \sum H_{r0}(n'_{a0} - n_a') = \sum n_i H_i = \sum n_i \int C_{pi} dT \tag{11}$$

With reference temperature at T_0, enthalpies $H_{io} = 0$

$$\Delta H_{r0} = \Delta H_{r298} + \int_{298}^{T_0} \Delta C_p dT \tag{12}$$

Substituting Eq. (12) into Eq. (10)

$$\left[-\Delta H_{r298} + \int_{298}^{T_0} \Delta C_p dT\right](n'_{a0} - n_a') = \sum n_i \int_{T_0}^{T} C_{pi} dT \tag{13}$$

Adiabatic process with $\Delta C_p = 0$ and with constant heat capacities

$$T = T_0 - \frac{\Delta H_{r298}(n'_{a0} - n_a')}{\sum n_i C_{pi}} \tag{14}$$

This expression is substituted instead of Eq. (8) to find the volume with Eq. (9)

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approximately by the Erlang statistical distribution which also is the result for an n-stage stirred tank battery,

$$E(t_r) = \frac{C}{C_0} = \frac{n^n t_r^{n-1}}{(n-1)!}\exp(-nt_r), \tag{17.11}$$

where n is the characterizing parameter; when n is not integral, $(n-1)!$ is replaced by the gamma function $\Gamma(n)$. C_0 is the initial average concentration. The variance,

$$\sigma^2 = \int_0^{\infty} E(t_r - 1)^2 dt_r = 1/n \tag{17.12}$$

of this distribution is a convenient single parameter characterization of the spread of residence times. This quantity also is related to the Peclet number, $\mathrm{Pe} = uL/D_e$, by

$$\sigma^2 = 2/\mathrm{Pe} - [1 - \exp(-\mathrm{Pe})]/\mathrm{Pe}^2, \tag{17.13}$$

where

u = linear velocity in the axial direction,
L = distance in the axial direction,
D_e = axial eddy diffusivity or dispersion coefficient.

At large values of Pe, the ratio Pe/n approaches 2.

The superficial Peclet number in packed beds,

$$\mathrm{Pe} = u_0 d_p / D_e$$

is very roughly correlated (Wen and Fan, 1975) in terms of the dimensionless groups $\mathrm{Re} = u_0 d_p \rho/\mu$ and $\mathrm{Sc} = \mu/\rho D_m$, where

d_p = particle diameter,
D_m = molecular diffusivity,
ε = fraction voids in the bed:

The correlations are

$$\varepsilon \mathrm{Pe} = 0.20 + 0.011\mathrm{Re}^{048}, \text{ for liquids, standard deviation } 46\%, \tag{17.14}$$

$$\frac{1}{\mathrm{Pe}} = \frac{0.3}{\mathrm{Re\,Sc}} + \frac{0.5}{1 + 3.8/\mathrm{Re\,Sc}}, \text{for gases.} \tag{17.15}$$

In Figure 17.1, the variance and its parameter n for a selection of commercial processes is shown. There are no direct correlations of

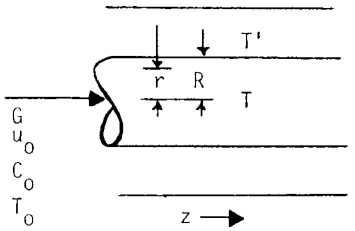
TABLE 17.7. Material and Energy Balances of a Packed Bed Reactor

Diffusivity and thermal conductivity are taken appreciable only in the radial direction
Material balance equation:

$$\frac{\partial x}{\partial z} - \frac{D}{u}\left(\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right) - \frac{\rho}{u_0 C_0} r_C = 0 \qquad (1)$$

Energy balance equation:

$$\frac{\partial T}{\partial z} - \frac{k}{GC_p}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \frac{\Delta H_r \rho}{GC_p} r_C = 0 \qquad (2)$$



At the inlet:

$$x(0, r) = x_0 \qquad (3)$$

$$T(0, r) = T_0 \qquad (4)$$

At the center:

$$r = 0, \frac{\partial x}{\partial r} = \frac{\partial T}{\partial r} = 0 \qquad (5)$$

At the wall:

$$r = R, \frac{\partial x}{\partial r} = 0 \qquad (6)$$

$$\frac{\partial T}{\partial r} = \frac{U}{k}(T' - T) \qquad (7)$$

When the temperature T' of the heat transfer medium is not constant, another enthalpy balance must be formulated to relate T' with the process temperature T.

A numerical solution of these equations may be obtained in terms of finite difference equivalents, taking m radial increments and n axial ones. With the following equivalents for the derivatives, the solution may be carried out by direct iteration:

$$r = m(\Delta r) \qquad z = n(\Delta z) \qquad (8)$$

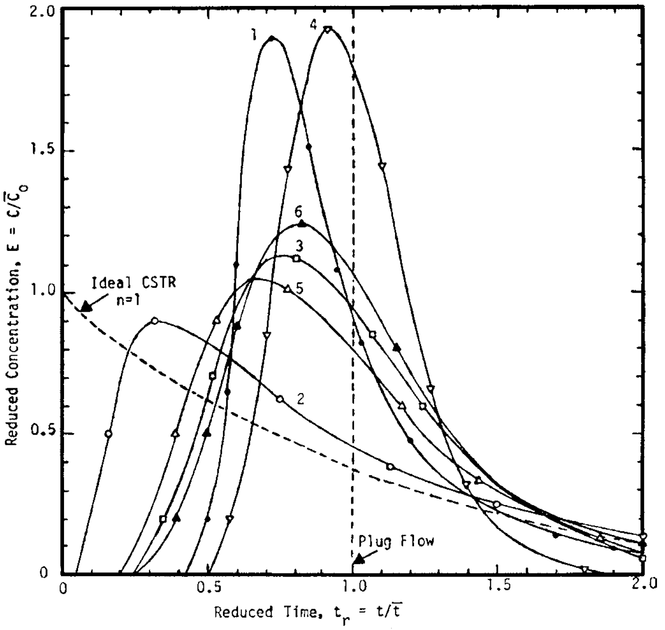
$$\frac{\partial T}{\partial z} = \frac{T_{m,n+1} - T_{m,n}}{\Delta z} \qquad (9)$$

$$\frac{\partial T}{\partial r} = \frac{T_{m+1,n} - T_{m,n}}{\Delta r} \qquad (10)$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}}{(\Delta r)^2} \qquad (11)$$

Expressions for the x-derivatives are of the same form:

r_c = rate of reaction, a function of s and T
G = mass flow rate, mass/(time)(superficial cross section)
U = linear velocity
D = diffusivity
K = thermal conductivity



No.	Code	Process	σ^2	n	Pe
1	○	aldolization of butyraldehyde	0.050	20.0	39.0
2	●	olefin oxonation pilot plant	0.663	1.5	1.4
3	□	hydrodesulfurization pilot plant	0.181	5.5	9.9
4	▽	low temp hydroisomerization pilot	0.046	21.6	42.2
5	△	commercial hydrofiner	0.251	4.0	6.8
6	▲	pilot plant hydrofiner	0.140	7.2	13.2

Figure 17.1. Residence time distributions of some commercial and pilot fixed bed reactors. The variance, the equivalent number of CSTR stages, and the Peclet number are given for each.

performance with respect to the geometry and the operating conditions in a vessel. The RTD has been of value as a diagnostic tool. For example, tracers injected with the reactants at the inlet to the reactor as well as other tracer concentrations are recorded as a function of time. The data obtained from these studies then are used to obtain the residence time of the feed in the reactor. Tracer data yield plots of the limits of chemical conversion and thus the reactor performance. Tracer response curves also yield information about poor distribution or bypassing of fluids which are indicators of poor performance. As a diagnostic tool, these studies lead to a better understanding of the flow behavior in the reactor. (Perry's, 8th ed.)

CONVERSION IN SEGREGATED AND MAXIMUM MIXED FLOWS

In some important cases, limiting models for chemical conversion are the segregated flow model represented by the equation

$$\overline{C}/C_0 = 1 - x = \int_0^\infty (C/C_0)_{\text{batch}} E(t_r)\,dt_r = \int_0^\infty (C/C_0)_{\text{batch}} E(t)\,dt \qquad (17.16)$$

and the maximum-mixedness model represented by Zwietering's equation. For a rate equation $r_c = kC^\alpha$ this equation is

$$\frac{dx}{dt_r} - kC_0^{\alpha-1}x^\alpha + \frac{E(t_r)}{1 - \int_0^{t_r} E(t_r)\,dt_r}x = 0, \qquad (17.17)$$

with the boundary condition

$$dx/dt_r = 0 \text{ when } t_r \to \infty, \qquad (17.18)$$

which is used to find the starting value x_∞ from

$$kC_0^{\alpha-1}x_\infty - \frac{E(t_r)}{1-\int_0^\infty E(t_r)dt_r}x_\infty = 0. \tag{17.19}$$

Numerical integration of the equation is sufficiently accurate by starting at $(x_\infty, t_r \simeq 4)$ and proceeding to $t_r = 0$ at which time the value of x is the conversion in the reactor with residence time distribution $E(t_r)$.

With a given RTD the two models may correspond to upper and lower limits of conversion or reactor sizes for simple rate equations; thus

	Conversion Limit	
Reaction Order	**Segregated**	**Max-Mix**
More than 1	upper	lower
Less than 1	lower	upper
Complex	?	?

Relative sizes of reactors based on the two models are given in Figure 17.2 for second- and half-order reactions at several conversions. For first-order reactions the ratio is unity. At small values of the parameter n and high conversions, the spread in reactor sizes is very large. In many packed bed operations, however, with proper initial distribution and redistribution the value of the parameter n is of the order of 20 or so, and the corresponding spread in reactor sizes is modest near conversions of about 90%. In such cases the larger predicted vessel size can be selected without undue economic hardship.

The data also can be rearranged to show the conversion limits for a reactor of a given size.

When the rate equation is complex, the values predicted by the two models are not necessarily limiting. Complexities can arise from multiple reactions, variation of density or pressure or temperature, incomplete mixing of feed streams, minimax rate behavior as in autocatalytic processes, and possibly other behaviors. Sensitivity of the reaction to the mixing pattern can be established in such cases, but the nature of the conversion limits will not be ascertained. Some other, possibly more realistic models will have to be devised to represent the reaction behavior. The literature has many examples of models but not really any correlations (Nauman and Buffham, 1983; Wen and Fan, 1975; Westerterp et al., 1984).

CONVERSION IN SEGREGATED FLOW AND CSTR BATTERIES

The mixing pattern in an n-stage CSTR battery is intermediate between segregated and maximum mixed flow and is characterized by residence time distribution with variance $\sigma^2 = 1/n$. Conversion in the CSTR battery is found by solving n successive equations

$$\frac{C_{j-1}}{C_0} = \frac{C_j}{C_0} + \frac{k\bar{t}}{n}C_0^{\alpha-1}\left(\frac{C_j}{C_0}\right)^\alpha \text{ for } j = 1-n \tag{17.20}$$

for $C_n/C_0 = 1 - x$. The ratio of required volumes of CSTR batteries and segregated flow reactors is represented by Figure 17.3 for several values of n over a range of conversions for a second-order reaction. Comparison with the maximum mixed/segregated flow relation of Figure 17.2 shows a distinct difference between the two sets of ratios.

DISPERSION MODEL

Although it also is subject to the limitations of a single characterizing parameter which is not well correlated, the Peclet number, the dispersion model predicts conversions or residence times unambiguously. For a reaction with rate equation $r_c = kC^\alpha$, this model is represented by the differential equation

$$\frac{1}{\text{Pe}}\frac{d^2x}{dz^2} - \frac{dx}{dz} + k\bar{t}C_0^{\alpha-1}(1-x)^\alpha = 0 \tag{17.21}$$

with the boundary conditions

$$\text{at } z = 0,\ \left(1 - x + \frac{1}{\text{Pe}}\frac{dx}{dz}\right)_0 = 1, \tag{17.22}$$

$$\text{at } z = 1,\ \frac{dx}{dz} = 0, \tag{17.23}$$

where

$x = 1 - C/C_0$, fractional conversion,
z = axial distance length of reactor.

An analytical solution can be found only for a first-order reaction. The two-point boundary condition requires a special numerical procedure. Plots of solutions for first- and second-order reactions are shown in Figures 17.4 and 17.5.

LAMINAR AND RELATED FLOW PATTERNS

A tubular reactor model that may apply to viscous fluids such as polymers has a radial distribution of linear velocities represented by

$$u = (1 + 2/m)\bar{u}(1 - \beta^m), \tag{17.24}$$

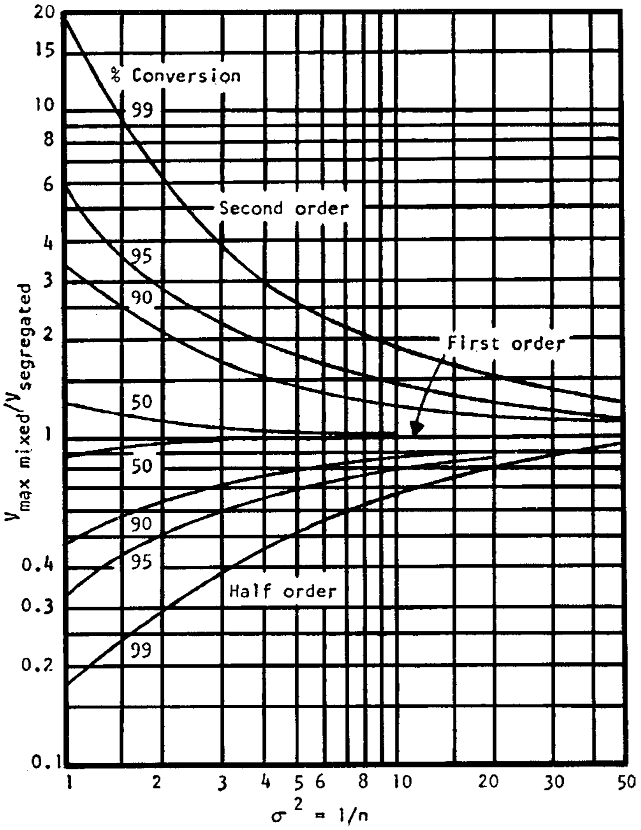


Figure 17.2. Relative volumes of maximum-mixed and segregated flow reactors with the same RTDs identified by $n = 1/\sigma^2$, as a function of conversion for second- and half-order reactions. For first-order reactions the ratio is unity throughout.

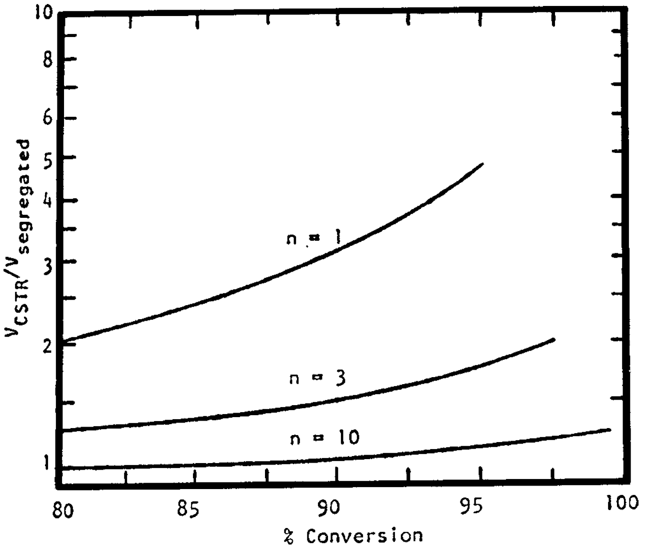


Figure 17.3. Ratio of volumes of an n-stage CSTR battery and a segregated flow reactor characterized by a residence time distribution with variance $\sigma^2 = 1/n$. Second-order reaction.

where $\beta = r/R$. When $m = 2$, the pattern is Poiseuille or laminar flow, and, when m is infinite, it is plug flow. The residence time along a streamline is

$$t = \bar{t}/(1 + 2/m)(1 - \beta^m). \tag{17.25}$$

The average conversion over all the streamlines is

$$\frac{\overline{C}}{C_0} = \frac{1}{\pi R^2}\int \left(\frac{C}{C_0}\right)_{\text{steamline}} d(\pi r^2) = 2\left(\frac{C}{C_0}\right)_{\text{steamline}} \beta d\beta. \tag{17.26}$$

For first-order reaction, for example

$$\frac{\overline{C}}{C_0} = 2\int_0^1 \exp\left[\frac{-k\bar{t}}{(1+2/m)(1-\beta^m)}\right]\beta d\beta \tag{17.27}$$

and for second-order

$$\frac{\overline{C}}{C_0} = 2\int_0^1 \frac{1}{1 + kC_0\bar{t}/(1+2/m)(1-\beta^m)}\beta d\beta. \tag{17.28}$$

These integrals must be evaluated numerically. Variation in residence time will contribute, for example, to the spread in molecular weight distribution of polymerizations.

17.5. SELECTION OF CATALYSTS

A catalyst is a substance that increases a rate of reaction by participating chemically in intermediate stages of reaction and is liberated near the end in a chemically unchanged form. Over a period of time, however, permanent changes in the catalyst—deactivation—may occur. Inhibitors are substances that retard rates of reaction. Many catalysts have specific actions in that they influence only one reaction or group of definite reactions. An outstanding example is the living cell in which there are several hundred different catalysts, called enzymes, each one favoring a specific chemical process.

The mechanism of a catalyzed reaction—the sequence of reactions leading from the initial reactants to the final products—is changed from that of the uncatalyzed process and results in a lower overall energy of activation, thus permitting a reduction in the temperature at which the process can proceed favorably. The equilibrium condition is not changed since both forward and reverse rates are accelerated equally. For example, a good hydrogenation catalyst also is a suitable dehydrogenation accelerator; the most favorable temperature will be different for each process, of course.

HOMOGENEOUS CATALYSTS

A convenient classification is into homogeneous and heterogeneous catalysts. The former types often are metal complexes that

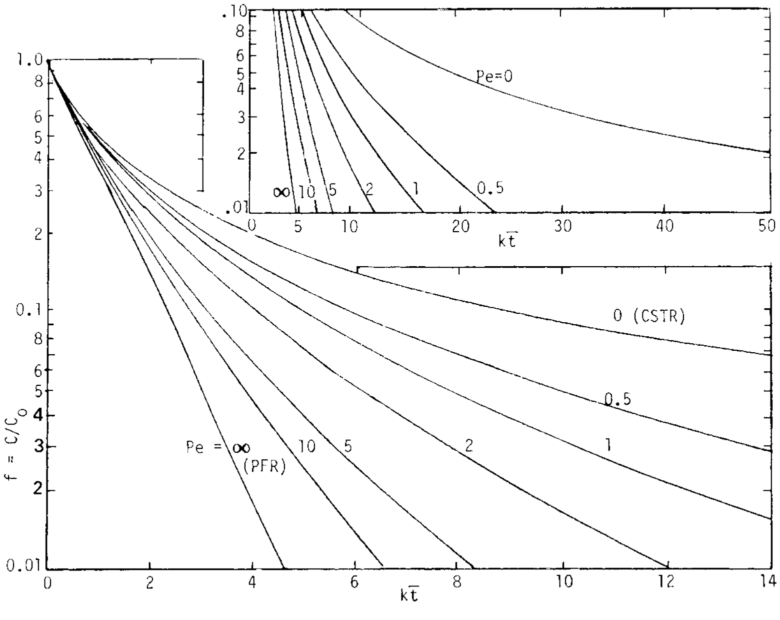


Figure 17.4. Dispersion model. Conversion of first-order reaction as function of the Peclet number.

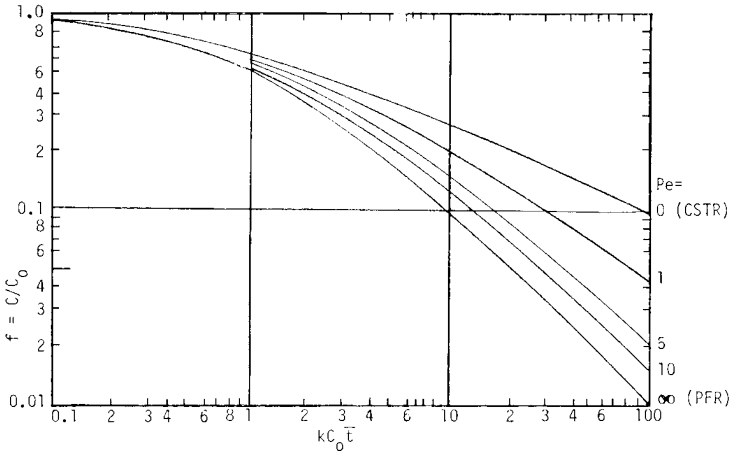


Figure 17.5. Second-order reaction with dispersion identified by the Peclet number, $\mathrm{Pe} = uL/D_L$.

are soluble in the reaction medium, but acids and bases likewise have a long known history of catalytic action. The specific action of a particular metal complex can be altered by varying the ligands or coordination number of the complex or the oxidation state of the central metal atom. Advantages of homogeneous catalysts are their specificity and low temperature and pressure requirements. Their main drawbacks are difficulty of recovery from the process fluid, often rapid degradation, and relatively high cost. Classic examples of homogeneous catalysis are the inversion of sugar with mineral acids, olefin alkylation with hydrofluoric acid, and the use of ammonia in the Solvay process and of nitrogen oxides in the Chamber process. A modern development is the synthesis of acetic acid from methanol and CO in the presence of homogeneous rhodium complexes.

The problem of separating the catalyst at the end of the operation can be eased in some cases by attaching the catalyst to a solid support, for instance, liquid phosphoric acid in the pores of a solid carrier for the vapor phase synthesis of cumene and the fairly wide application of enzymes that are attached (immobilized) by various means to solid polymers. Some metal ligands also are being combined with solid polymers.

HETEROGENEOUS CATALYSTS

By far the greatest tonnages of synthetic chemicals are manufactured in fluid phases with solid catalysts. Such materials are cheap, are easily separated from the reaction medium, and are adaptable to either flow or nonflow reactors. Their drawbacks are a lack of specificity and often high temperature and pressure requirements. The principal components of most heterogeneous catalysts are three in number:

1. A catalytically active substance or mixture.
2. A carrier of more or less large specific surface on which the catalyst proper is deposited as a thin film, either for economy when the catalyst is expensive or when the catalyst itself cannot be prepared with a suitable specific surface.
3. Promoters, usually present in relatively small amount, which enhance the activity or retard degradation.

Some composite catalysts are designed to promote several reactions of a sequence leading to the final products. A basic catalyst often can be selected with general principles, but subsequent fine tuning of a commercially attractive design must be done in a pilot plant or sometimes on a plant scale.

Catalyst design is a broad field beginning with fundamentals like those reported by Trimm (1980) or by using analogies to what has been effective in chemically similar problems. Scientific basis for catalyst selection is a continually developing field. The classic literature reported by Roiter (1968–1985) on catalyst design, industrial catalyst practice as well as specific processes and general aspects of catalysis are covered by Leach (1983–1985), Satterfield (1980) has described industrial catalytic processes and through the intervening years has remained active in the subject area.

Industrial cracking, reforming, partial oxidation, hydrodesulfurization, and catalysis by transition-metal complexes are treated in detail by Gates et al. (1979) and the catalytic conversion of hydrocarbons by Pines (1981). The mechanisms and other aspects of organic catalysis are described in one of the volumes of the series edited by Bamford and Tipper (1978). A vast literature exists for enzyme processes; that technology is well reviewed in two articles in *Ullmann's Encyclopedia* (Biotechnologie, Enzyme) as well as by Bailey and Ollis (1986). In the present text, Table 17.1 identifies the catalyst used in most of the 100 processes listed.

Intermediate processes of catalyzed organic reactions may involve neutral free radicals $R^{\cdot}$, positive ions R^+, or negative ions R^- as short-lived reactants. A classification of catalysts and processes from the point of view of elementary reactions between reagents and catalysts is logically desirable but has not yet been worked out. However, there is a wealth of practice more or less completely documented, some proprietary but available at a price. The ensuing discussions are classified into kinds of catalysts and into kinds of processes.

KINDS OF CATALYSTS

To a certain extent, it is known what kinds of reactions are speeded up by certain classes of catalysts, but individual members of the same class may differ greatly in activity, selectivity, resistance to degradation, and cost. Even small differences in these properties can mean large sums of money on the commercial scale. Solid catalysts, the most usual kind, are not particularly specific or selective, so that there is a considerable crossing of lines in classifications between kinds of catalysts and kinds of reactions they favor. Nevertheless, leading relations can be brought out.

Strong acids are able to donate protons to a reactant and to take them back. Into this class fall the common acids, aluminum halides, and boron trifluoride. Also acid in nature are silica, alumina, aluminosilicates, metal sulfates and phosphates, and sulfonated ion exchange resins. The nature of the active sites on these kinds of solids still is not completely understood. The majority of reactions listed subsequently are catalytically influenced to some extent by acidic substances. Zeolites are dehydrated aluminosilicates with small pores of narrow size distribution, to which is due their highly selective catalytic action since only molecules small enough to enter the pores can react. In cracking operations they are diluted to 10–15% in silica-alumina to restrain their great activity; the composite catalyst still is very active but makes less carbon, makes lower amounts of C_3–C_4 products, and has a longer life. Their greater activity has led to the supplanting of fluidized bed crackers by riser-tube reactors. When zeolites are incorporated in reforming catalysts, they crack isoparaffins into straight chains that enter the pores and convert into higher octane substances.

Base catalysis is most effective with alkali metals dispersed on solid supports or in the homogeneous form as aldoxides, amides, and so on. Small amounts of promoters may be added to form organoalkali compounds that really have the catalytic power. Basic ion exchange resins also are useful. Some base-catalyzed processes are isomerization and oligomerization of olefins, reaction of olefins with aromatics, and hydrogenation of polynuclear aromatics.

Metal oxides, sulfides, and hydrides form a transition between acid-base and metal catalysts. They catalyze hydrogenation-dehydrogenation as well as many of the reactions catalyzed by acids such as cracking and isomerization. Their oxidation activity is related to the possibility of two valence states which allow oxygen to be released and reabsorbed alternately. Common examples are oxides of cobalt, iron, zinc, and chromium; and hydrides of precious metals which can release hydrogen readily. Sulfide catalysts are more resistant than metallic catalysts to formation of coke deposits and to poisoning by sulfur compounds; their main application is to hydrodesulfurization.

Metals and alloys. The principal industrial metallic catalysts are found in periodic group VIII which are transition elements with almost completed 3d, 4d, and 5d electron orbits. According to one theory, electrons from adsorbed molecules can fill the vacancies in the incomplete shells and thus make a chemical bond. What happens subsequently will depend on the operating conditions. Platinum, palladium, and nickel, for example, form both hydrides and oxides; they are effective in hydrogenation (vegetable oils, for instance) and oxidation (ammonia or sulfur dioxide, for instance). Alloys do not always have catalytic properties intermediate between those of the pure metals since the surface condition may be different from the bulk and the activity is a property of the surface. Addition of small amounts of rhenium to Pt/Al_2O_3 results in a smaller decline of activity with higher temperature and slower deactivation rate. The mechanism of catalysis by alloys is in many instances still controversial.

Transition-metal organometallic catalysts in solution are effective for hydrogenation at much lower temperatures than metals such as platinum. They are used for the reactions of carbon monoxide with olefins (hydroformylation) and for some oligomerizations. The problem of separating the catalyst from solution sometimes is avoided by anchoring or immobilizing the catalyst on a polymer support containing pendant phosphine groups and in other ways.

KINDS OF CATALYZED ORGANIC REACTIONS

A fundamental classification of organic reactions is possible on the basis of the kinds of bonds that are formed and destroyed and the natures of eliminations, substitutions, and additions of groups. Here a more pragmatic list of 20 commercially important individual kinds or classes of reactions will be discussed.

1. Alkylations, for example, of olefins with aromatics or isoparaffins, are catalyzed by sulfuric acid, hydrofluoric acid, BF3, and AlCl3.
2. Condensations of aldehydes and ketones are catalyzed homogeneously by acids and bases, but solid bases are preferred, such as anion exchange resins and alkali or alkaline earth hydroxides or phosphates.
3. Cracking, a rupturing of carbon-carbon bonds, for example, of gas oils to gasoline, is favored by silica-alumina, zeolites, and acid types generally.
4. Dehydration and dehydrogenation combined utilizes dehydration agents combined with mild dehydrogenation agents. Included in this class of catalysts are phosphoric acid, silica-magnesia, silica-alumina, alumina derived from aluminum chloride, and various metal oxides.
5. Esterification and etherification may be accomplished by catalysis with mineral acids of BF3; the reaction of isobutylene with methanol to make MTBE is catalyzed by a sulfonated ion exchange resin.
6. Fischer-Tropsch oligomerization of CO + hydrogen to make hydrocarbons and oxygenated compounds. Iron promoted by potassium is favored, but the original catalyst was cobalt which formed a carbonyl in process.
7. Halogenation and dehalogenation are catalyzed by substances that exist in more than one valence state and are able to accept and donate halogens freely. Silver and copper halides are used for gas-phase reactions, and ferric chloride commonly for liquid phase. Hydrochlorination (the absorption of HCl) is promoted by BiCl3 or SbCl3 and hydrofluorination by sodium fluoride or chromia catalysts that fluoride under reaction conditions. Mercuric chloride promotes addition of HCl to acetylene to make vinyl chloride.
8. Hydration and dehydration employ catalysts that have a strong affinity for water. Alumina is the principal catalyst, but also used are aluminosilicates, metal salts, and phosphoric acid or its metal salts on carriers and cation exchange resins.
9. Hydrocracking is catalyzed by substances that promote cracking and hydrogenation together. Nickel and tungsten sulfides on acid supports and zeolites loaded with palladium are used commercially.
10. Hydrodealkylation, for example, of toluene to benzene, is promoted by chromia-alumina with a low sodium content.
11. Hydrodesulfurization uses sulfided cobalt/molybdena/alumina, or alternately with nickel and tungsten substituted for Co and Mo.
12. Hydroformylation, or the oxo process, is the reaction of olefins with CO and hydrogen to make aldehydes. The catalyst base is cobalt naphthenate which transforms to cobalt hydrocarbonyl in place. A rhodium complex that is more stable and functions at a lower temperature also is used.
13. Hydrogenation and dehydrogenation employ catalysts that form unstable surface hydrides. Transition-group and bordering metals such as Ni, Fe, Co, and Pt are suitable, as well as transition group oxides or sulfides. This class of reactions includes the important examples of ammonia and methanol syntheses, the Fischer-Tropsch and oxo and synthol processes and the production of alcohols, aldehydes, ketones, amines, and edible oils.
14. Hydrolysis of esters is accelerated by both acids and bases. Soluble alkylaryl sulfonic acids or sulfonated ion exchange resins are satisfactory.

15. Isomerization is promoted by either acids or bases. Higher alkylbenzenes are isomerized in the presence of AlCl3/HCl or BF3/HF; olefins with most mineral acids, acid salts, and silica alumina; saturated hydrocarbons with AlCl3 or AlBr3 promoted by 0.1% of olefins.
16. Metathesis is the rupture and reformation of carbon-carbon bonds, for example of propylene into ethylene plus butene. Catalysts are oxides, carbonyls or sulfides of Mo, W, or rhenium.
17. Oxidation catalysts are either metals that chemisorb oxygen readily such as platinum or silver, or transition metal oxides that are able to give and take oxygen by reason of their having several possible oxidation states. Ethylene oxide is formed with silver, ammonia is oxidized with platinum, and silver or copper in the form of metal screens catalyze the oxidation of methanol to formaldehyde.
18. Polymerization of olefins such as styrene is promoted by acid or base catalysts or sodium; polyethylene is made with homogeneous peroxides.
19. Reforming is the conversion primarily of naphthenes and alkanes to aromatics, but other chemical reactions also occur under commercial conditions. Platinum or platinum/rhenium are the hydrogenation-dehydrogenation component of the catalyst and alumina is the acid component responsible for skeletal rearrangements.
20. Steam reforming is the reaction of steam with hydrocarbons to make a manufactured gas containing mostly methane with trace amounts of ethylene, ethane, and hydrogen. For the manufacture of this gas, a representative catalyst composition contains 13 wt % Ni, 12.1 wt % U, and 0.3 wt % K; it is particularly resistant to poisoning by sulfur. To make hydrogen, the catalyst contains oxides of Ni, Ca, Si, Al, Mg, and K. Specific formulations are given by Satterfield (1980).

PHYSICAL CHARACTERISTICS OF SOLID CATALYSTS

Although a few very active solid catalysts are used as fine wire mesh or other finely divided form, catalysts are mostly porous bodies whose total surface is measured in m^2/g. These and other data of some commercial catalysts are shown in Table 17.8. The physical characteristics of major importance are as follows:

1. *Particle size*. In gas fluidized beds the particle diameters average less than 0.1 mm; smaller sizes impose too severe loading on entrainment recovery equipment. In slurry beds the particles can be about 1 mm dia. In fixed beds the range is 2–5 mm dia. The competing factors are that the pressure drop increases with diminishing diameter and the accessibility of the internal surface decreases with increasing diameter. With poorly thermally conducting materials, severe temperature gradients or peaks arise with large particles that may lead to poor control of the reaction and the development of undesirable side reactions like carbonization.
2. *Specific surface*. Solid spheres of 0.1 mm dia have a specific surface of $0.06\,m^2/mL$ and an activated alumina one of about $600\,m^2/mL$. Other considerations aside, a large surface is desirable because the rate of reaction is proportional to the amount of accessible surface. Large specific surfaces are associated with pores of small diameters and are substantially all internal surface.
3. *Pore diameters and their distribution*. Small pores limit accessibility of internal surface because of increased resistance to diffusion of reactants into the pores. Diffusion of products outward also is slowed down and may result in degradation of those products. When the catalyst is expensive, the inaccessible internal surface is a liability. A more or less uniform pore diameter is desirable, but the distribution usually is statistical and only molecular sieves have nearly uniform pores. Those catalyst granules that are extrudates of compacted masses of smaller particles have bimodal pore size distribution, between the particles and within them. Clearly a compromise between large specific surface and its accessibility as measured by pore diameter is required in some situations.
4. *Effective diffusivity*. Resistance to diffusion in a catalyst pore is due to collisions with other molecules and with the walls of the pore. The corresponding diffusivities are called bulk diffusivity and Knudsen diffusivity DK. Many data and correlations of the former type exist; the latter is calculable from the following equation (Satterfield, 1970, p. 42):

$$D_K = \frac{19,400\theta^2}{S_g \rho_p}\left(\frac{T}{M}\right)^{1/2}, \tag{17.29}$$

where

θ = fraction porosity,
S_g = specific surface per unit mass,
ρ_p = density,
T = temperature (K),
M = molecular weight.

This equation applies to uniform cylindrical pores whose length equals the thickness of the catalyst through which the diffusion takes place. The actual diffusivity in common porous catalysts usually is intermediate between bulk and Knudsen. Moreover, it depends on the pore size distribution and on the true length of path. Two tortuosity factors are defined:

τ_p = ratio of measured diffusivity to that calculated with the known pore size distribution and bulk diffusivity and the thickness of the catalyst mass.
τ_m = ratio of measured diffusivity to that calculated from the Knudsen formula with a mean pore diameter.

The data of Table 17.8 exhibit a fairly narrow range of τ_p, an average of about 4, but there seems to be no pattern to τ_m, which is not surprising since the diffusions actually are intermediate between bulk and Knudsen in these cases. In order to be able to calculate the effective diffusivity, it is necessary to know the pore size distribution, the specific surface, the porosity, and bulk diffusivity in the reaction mixture under reaction conditions. Such a calculation is primarily of theoretical interest. Practically it is more useful to simply measure the diffusivity directly, or even better to measure the really pertinent property of catalyst effectiveness as defined next.

CATALYST EFFECTIVENESS

Catalyst effectiveness is a measure of the extent of utilization of internal surface; it is the ratio of a rate of reaction actually achieved with the catalyst particle to the rate that would prevail if all of the internal surface were exposed to the reactant concentration at the external surface of the particle. The rate equation accordingly is modified to

$$r = knf(C_s), \tag{17.30}$$

where η is the catalyst effectiveness and C_s is the concentration of the reactant at the external surface. For isothermal reactions, η always is less than unity, but very large values can develop for exothermic reactions in poorly conducting catalysts.

TABLE 17.8. Physical Properties of Some Commercial Catalysts and Carriers[a]

Designation	Nominal Size	Surface Area (m2/g)	Total Void Fraction	$D^{b}_{eff}\times 10^3$ (cm^2/sec)	Average Tortuosity Factor T_p Parallel-Path Pore Model	$r_e = 2V_e/S_e$(Å)	τm Based on Average Pore Radius
T-126	3/16 × 1/8 in.	197	0.384	29.3	3.7±0.2	29	0.45
T-1258		302	0.478	33.1	3.8±0.2	23.6	0.41
T-826		232	0.389	37.7	3.9±0.1	21.4	0.26
T-314		142	0.488	20.0	7.1±0.9	41.5	1.2
T-310		154	0.410	16.6	3.8 + 0.1	34.3	0.67
G-39	3/16 × 3/16 in.	190	0.354	17.5	4.8±0.3	22.4	0.53
G-35		—	0.354	18.2	4.9±0.1		—
T-606		—	0.115	27.7	2.9±0.2		—
G-58		6.4	0.389	87.0	2.8±0.3	543	2.87
T-126	1/4 × 1/4 in.	165	0.527	38.8	3.6±0.3	49.0	0.79
T-606		—	0.092	0.71	79±28		—
G-41		—	0.447	21.9	4.4±0.1		—
G-52		—	0.436	27.4	3.9 + 0.2		—
G-56	1/2 × 1/2 in.	42	0.304	8.1	11.1±1.1	84	3.74
BASF	5 × 5 mm	87.3	0.500	11.8	7.3 + 0.7	41	2.05
Harshaw	1/4 × 1/4 in.	44	0.489	13.3	7.2±0.1	91	3.95
Haldor Topsøe	1/4 × 1/4 in.	143	0.433	15.8[e]	2.8	25.8	0.83

Catalyst	Description
T–126	Activated γ-alumina
T-1258	Activated γ-alumina
T-826	3% CoO, 10% MoO3, and 3% NiO on alumina
T-314	About 8–10% Ni and Cr in the form of oxides on an activated alumina
T-310	About 10–12% nickel as the oxide on an activated alumina
T-606	Specially compounded refractory oxide support
G-39	A cobalt-molybdenum catalyst, used for simultaneous hydrodesulfurization of sulfur compounds and hydrogenation of olefins
G-35	A cobalt-molybdenum catalyst supported on high-purity alumina, used for hydrodesulfurization of organic sulfur compounds
G-41	A chromia-alumina catalyst, used for hydrodealkylation and dehydrogenation reactions
G-58	Palladium-on-alumina catalyst, for selective hydrogenation of acetylene in ethylene
G-52	Approximately 33wt % nickel on a refractory oxide support, prereduced. Used for oxygen removal from hydrogen and inert gas streams
G-56	A nickel-base catalyst used for steam reforming of hydrocarbons
BASF	A methanol synthesis catalyst, prereduced
Harshaw	A methanol synthesis catalyst, prereduced
Haldor Topsøe	A methanol synthesis catalyst, prereduced

[a]The measured effective diffusivities are those of hydrogen in nitrogen at room temperature and pressure except that of Haldor Topsoe which is of helium in nitrogen.
(Satterfield and Cadle, 1968).

A great deal of attention has been devoted to this topic because of the interesting and often solvable mathematical problems that it presents. Results of such calculations for isothermal zero-, first-, and second-order reactions in uniform cylindrical pores are summarized in Figure 17.6. The abscissa is a modified Thiele modulus whose basic definition is

$$\phi = R/k_v C_s^{n-1}/D_{\text{eff}}, \tag{17.31}$$

where R is a linear dimension (the radius of a sphere, for example), k_v the specific rate on a volumetric basis, C_s the surface concentration, n the order of the reaction, and D_{eff} the effective diffusivity. For nonisothermal reactions, those with variable volume and with rate equations of the Langmuir-Hinshelwood or other complex types, additional parameters are involved. Although such calculations can be made, they still require measurements of effective diffusivity as well as a number of unverifiable assumptions. Accordingly in practical cases it is preferable to make direct measurements of catalyst effectiveness and to correlate them with operating parameters. The effectiveness is deduced by comparing conversion with the reference particle size with those with successively small particle sizes until the effect disappears. Two examples are presented to illustrate the variables that are taken into account and the magnitudes of the effects.

For synthesis of ammonia the effectiveness has been measured by Dyson and Simon (1968) and correlated by the equation

$$\eta = b_0 + b_1 T + b_2 x + b_3 T^2 + b_4 x^2 + b_5 T^3 + b_6 x^3, \tag{17.32}$$

where T is in K, x is fractional conversion of nitrogen, and the bi depend on pressure as given in this table:

Pressure (atm)	b_0	b_1	b_2	b_3	b_4	b_5	b_6
150	−17.539096	0.07697849	6.900548	-1.082790×10^{-4}	−26.42469	4.927648×10^{-3}	38.93727
225	−8.2125534	0.03774149	6.190112	-5.354571×10^{-5}	−20.86963	2.379142×10^{-3}	27.88403
300	−4.6757259	0.02354872	4.687353	-3.463308×10^{-5}	−11.28031	1.540881×10^{-3}	10.46627

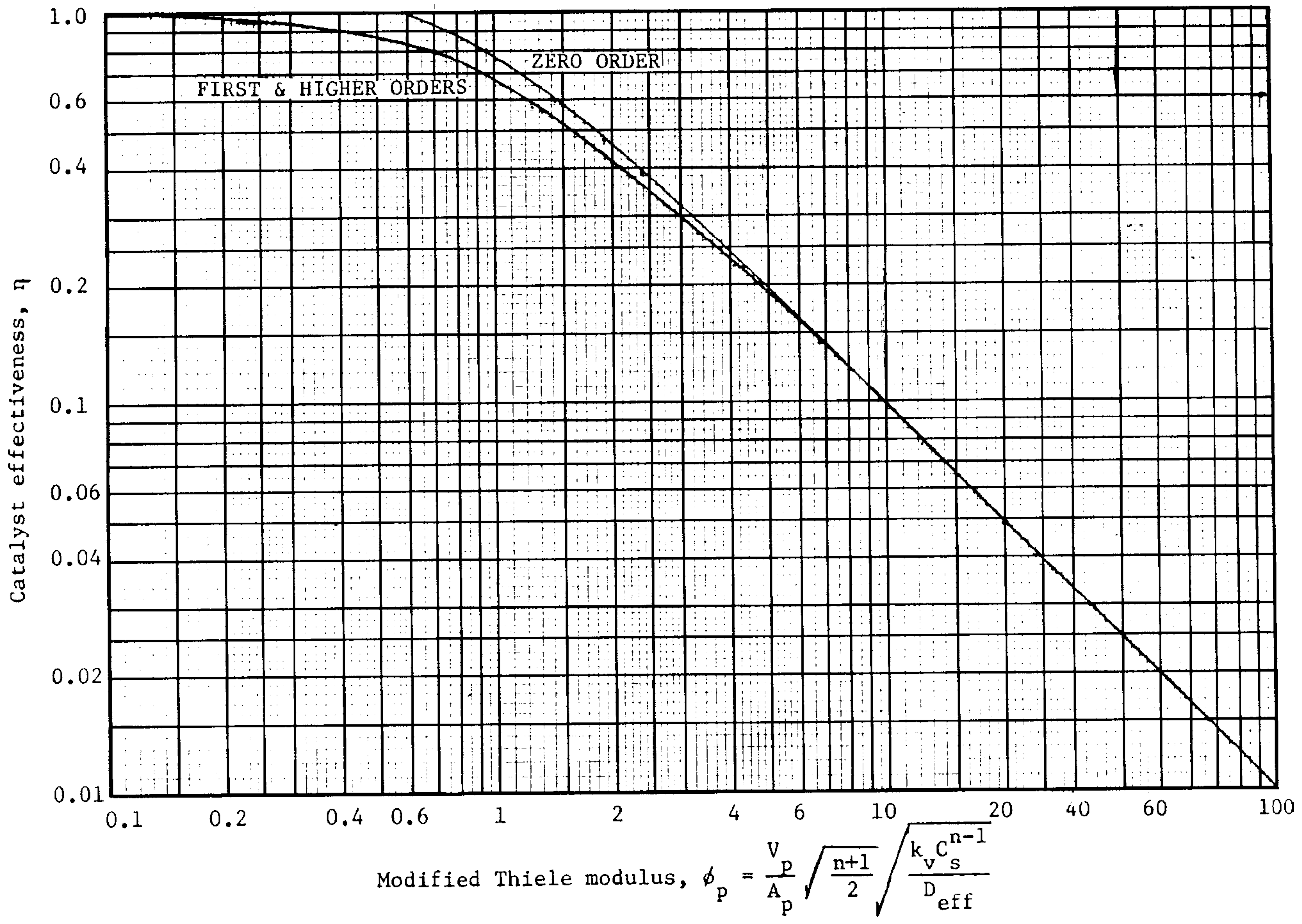


Figure 17.6. Generalized chart of catalyst effectiveness for reactions of order n in particles with external surface A_p and volume V_p. The upper curve applies exactly to zero-order reaction in spheres, and the lower one closely for first- and second-order reactions in spheres. (Walas, 1988).

The reference mixture has $H_2/N_2 = 3$ and contains 12.7% inert; other ratios had slightly different effectiveness. The particle diameters are 6–10 mm. Some calculations from this equation at 225 atm are:

T	x	η
700	0.25	0.81
700	0.10	0.57
650	0.25	0.91

For oxidation of sulfur dioxide, measurements of effectiveness were made by Kadlec et al. (1968) whose data are shown following. They are at atmospheric pressure. The initial content of SO_2 and the conversion have little effect on the result. Both increase in size of granule and temperature lower the effectiveness, although the effect of temperature is somewhat erratic.

The rate equations of both these processes are quite complex, and there is little likelihood that the effectiveness could be deduced mathematically from fundamental data as functions of temperature, pressure, conversion, and composition, which is the kind of information needed for practical purposes. Perhaps the only estimate that can be made safely is that, in the particle size range below 1 mm or so, the effectiveness probably is unity. The penetration of small pores by liquids is slight so that the catalysts used in liquid slurry systems are of the low specific surface type or even nonporous.

Experimentally Determined Effectiveness Factors

		Conversion					
°C	% SO_2	0.4	0.5	0.6	0.7	0.8	0.9
Irregular grain shape, fraction 5–6 mm							
460	7	0.84	0.84	0.82	0.83	0.82	0.81
480	7	0.60	0.62	0.62	0.62	0.60	0.60
500	7	—	0.54	0.51	0.50	0.50	0.52
520	7	—	0.35	0.35	0.35	0.38	0.38
Cylindrical granules of 6 mm diameter and 12 mm length							
460	7	0.57	0.57	0.59	0.60	0.60	0.60
	10	0.58	0.62	0.63	0.63	0.62	0.62
480	7	0.53	0.54	0.56	0.57	0.56	0.57
	10	0.44	0.45	0.45	0.46	0.45	0.47
500	7	0.25	0.25	0.27	0.28	0.27	0.31
	10	0.26	0.27	0.30	0.30	0.31	0.30
520	7	—	0.21	0.21	0.22	0.22	0.23
	10	—	0.20	0.21	0.21	0.22	0.24

17.6. TYPES AND EXAMPLES OF REACTORS

In chemical manufacturing operations, the reactor is the central equipment item of the plant. Cusak (1999, 1999, 2000) wrote three articles that provide an overview of reactor selection and design. The first article (Cusak, October 1999) is a summary of reaction engineering principles and points out that the selection and design of the reactor can benefit from insights obtained from the engineering of separation processes. In this article, the author also suggests the consideration of space time and space velocity in reactor selection. Cusak (December 1999) discussed the major type of reactors, e.g. CSTR, plug flow back mix, etc. presenting the advantages and disadvantages of each. The last article in the series (Cusak, 2000) is concerned with the optimization of design and the operation of chemical reactors. He cautions that the engineer must take into account departures from ideality like fluid short-circuiting, channeling, axial flow and dispersion as well as the presence of stagnation zones.

These three articles serve as refreshers for the practicing engineer who may need some technical review before attempting to design reactors for specific applications.

Seve (1997, 1998, 1999, 2000) wrote a series of articles that provide basic information for the design and operation of chemical reactors. These together with the Cusak articles provide a review of the design of commercial chemical plant reactors. These two sets of articles are recommended to the process engineer as another viewpoint for designing reactors.

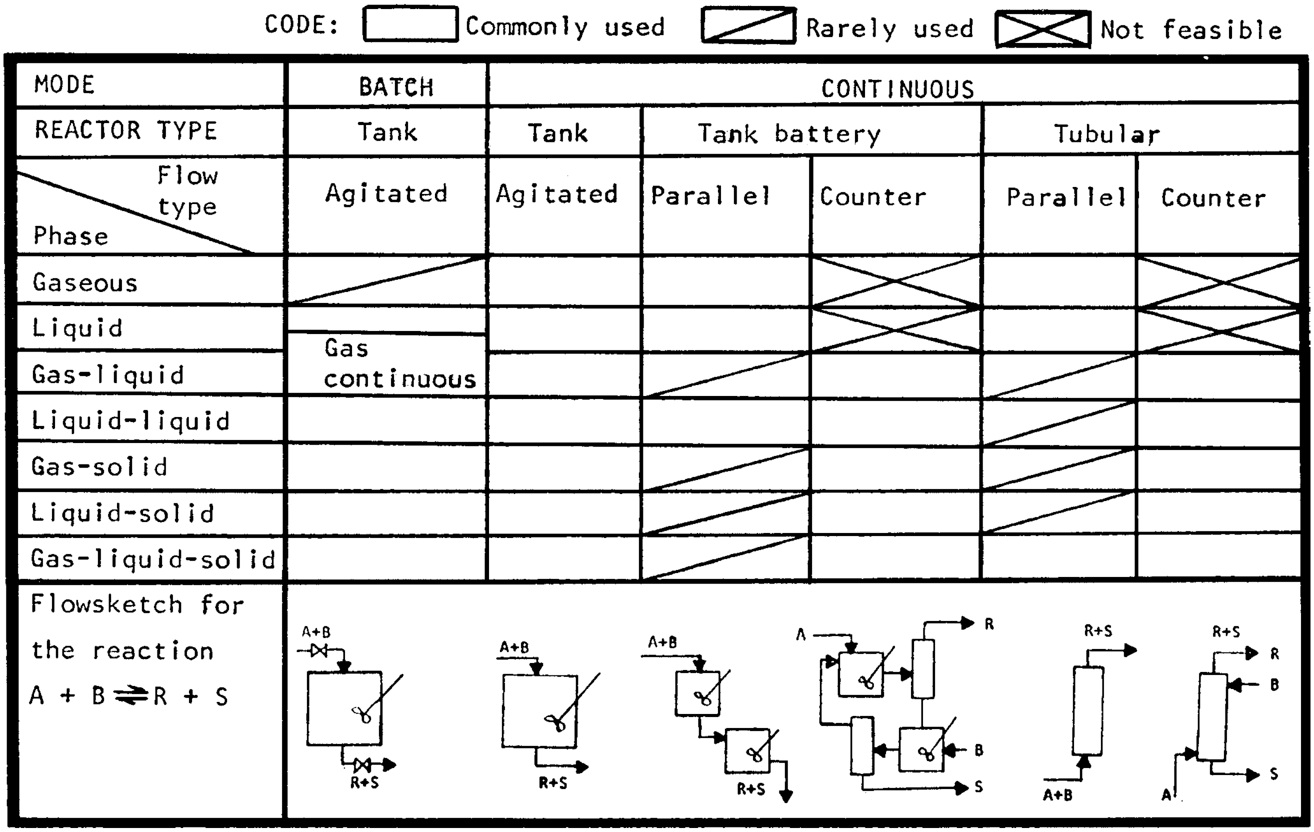
There are two basic vessel types of chemical reactors, namely tank and pipe. They are both used in a batch or continuous mode. Generally they are run at steady state but also can be operated in a transient mode. When a reactor has been off line and is brought back into operation, it might be considered to be in a transient state initially. Industrially, there are three main basic models used to study process variables of different chemical reactors: batch reactor model, continuous stirred-tank model and the plug-flow reactor. Catalytic reactors may be of the same basic model types but require special attention for some of the assumptions used for non-catalytic reactors may not apply. In these reactors, the analysis is very complicated due to the catalysts reacting with the reagents in a flow process. Reagents must diffuse into the catalyst and the products must exit. Perfect mixing cannot be assumed and the reaction path may be multistep with intermediates that need to be removed as they form.

Almost every kind of holding or contacting equipment has been used as a chemical reactor at some time, from mixing nozzles and centrifugal pumps to the most elaborate towers and tube assemblies. This section is devoted to the general characteristics of the main kinds of reactors, and also provides a gallery of selected examples of working reactors.

The most obvious distinctions are between nonflow (batch) and continuous operating modes and between the kinds of phases that are being contacted. A classification of appropriate kinds of reactors on the basis of these two sets of distinctions is in Figure 17.7.

When heterogeneous mixtures are involved, the conversion rate often is limited by the rate of interphase mass transfer, so that a large interfacial surface is desirable. Thus, solid reactants or catalysts are finely divided, and fluid contacting is forced with mechanical agitation or in packed or tray towers or in centrifugal pumps. The rapid transfer of reactants past heat transfer surfaces by agitation or pumping enhances also heat transfer and reduces harmful temperature gradients.

Batch processing is used primarily when the reaction time is long or the required daily production is small. Batch reactors are commonly used in the fine chemical and pharmaceutical industries where



CODE: ☐ Commonly used ◪ Rarely used ☒ Not feasible

MODE	BATCH	CONTINUOUS				
REACTOR TYPE	Tank	Tank	Tank battery		Tubular	
Phase \ Flow type	Agitated	Agitated	Parallel	Counter	Parallel	Counter
Gaseous	◪	☐	☐	☒	☐	☒
Liquid	☐	☐	☐	☒	☐	☒
Gas-liquid	Gas continuous	☐	◪	☐	◪	☐
Liquid-liquid	☐	☐	☐	☐	◪	☐
Gas-solid	☐	☐	◪	☐	◪	☐
Liquid-solid	☐	☐	◪	☐	◪	☐
Gas-liquid-solid	☐	☐	◪	☐	☐	☐
Flowsketch for the reaction A + B ⇄ R + S						

Figure 17.7. Classification of reactors according to the mode of operation and the kinds of phases involved.

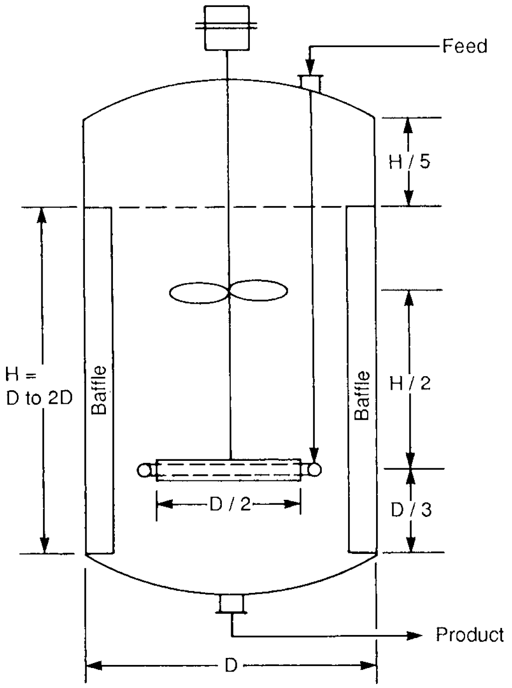


Figure 17.8. Typical proportions of a stirred tank reactor with radial and axial impellers, four baffles, and a sparger feed inlet.

they have been the workhorse. They perform many different unit operation tasks such as chemical reactions, biochemical reactions, crystallizations, distillation and dissolution (Ashe et al., 2008).

Otherwise, it is not possible to generalize as to the economical transition point from batch to continuous operation. One or more batch reactors together with appropriate surge tanks may be used to simulate continuous operation on a daily or longer basis.

BATCH PROCESSING

Stirred Tanks

Stirred tanks are the most common type of batch reactor. Typical proportions are shown on Figures 17.8 and 10.1, and modes of level control on Figure 3.6. Stirring is used to mix the ingredients initially, to maintain homogeneity during reaction, and to enhance heat transfer at a jacket wall or internal surfaces. The reactor of Figure 17.9(b) employs a pumparound for mixing of the tank contents and for heat transfer in an external exchanger. Pumparound or recycle in general may be used to adapt other kinds of vessels to service as batch mode reactors; for example, any of the packed vessels of Figure 17.13 (a)–(e). A pumparound tubular flow reactor is employed for the polymerization of ethylene. As the polymer is formed, it is bled off at a much lower rate than that of the recirculation, so that in a sense the action of this equipment approaches batch operation.

Some special industrial stirred reactors are illustrated in Figure 17.10: (b) is suitable for pasty materials, (c) for viscous materials, and the high recirculation rate of (d) is suited to intimate contacting of immiscible liquids such as hydrocarbons with aqueous solutions.

CONTINUOUS PROCESSING

Many applications of stirred tank reactors are to continuous processing, either with single tanks or multiple arrangements as in Figures 17.9(c)–(d). Knowledge of the extent to which a stirred tank does approach complete mixing is essential to being able to predict its performance as a reactor. The other limiting case is that of plug flow, in which all nonreacting molecules have the same residence time. Deviations from the limiting cases of complete mixing (in a CISTR) and no axial mixing (in a PFR) are evaluated with residence time distributions (RTDs) based on analyses of tracer tests.

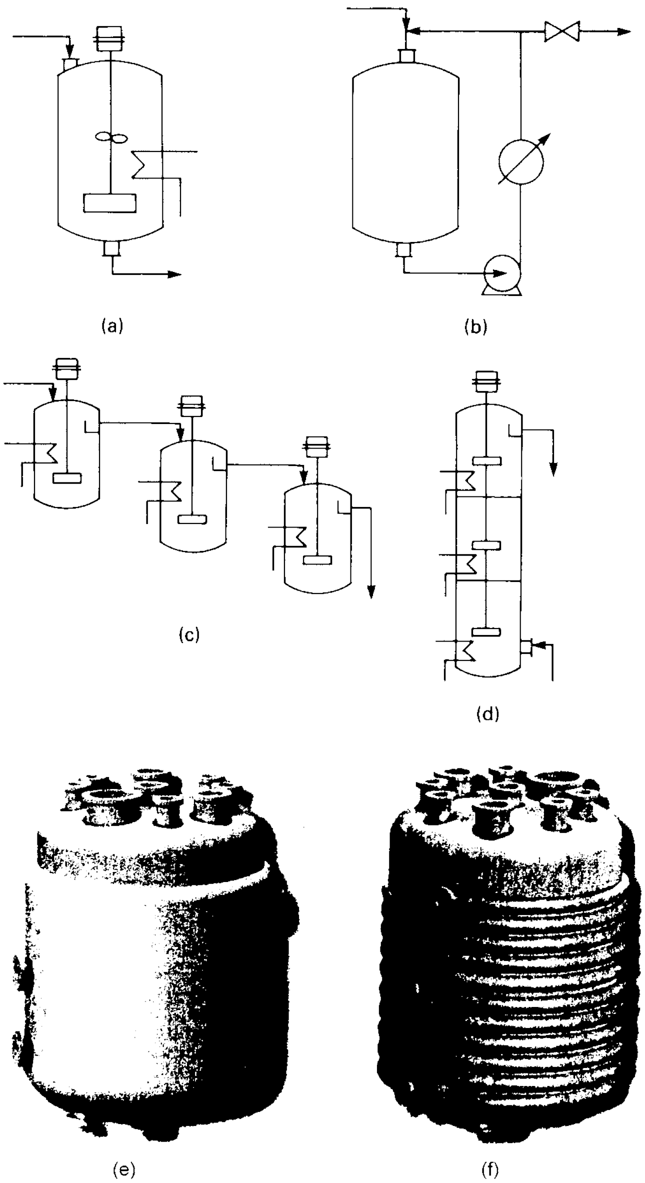


Figure 17.9. Stirred tank reactors, batch and continuous. (a) With agitator and internal heat transfer surface, batch or continuous. (b) With pumparound mixing and external heat transfer surface, batch or continuous. (c) Three-stage continuous stirred tank reactor battery. (d) Three-stage continuous stirred tank battery in a single shell. (Walas, 1988) (e) Conventional batch reactor with single jacket. (f) Batch reactor with half coil jacket (Ashe et al., 2008).

As mentioned earlier in this section, although much research and engineering has been directed toward correlating RTD behavior with operating and design factors, successful results generally have not been attained.

The behavior of the CSTR is frequently modeled by a Continuous Ideal Stirred-Tank Reactor (CISTR) but the major assumption used in the calculations is perfect mixing. That assumption is only

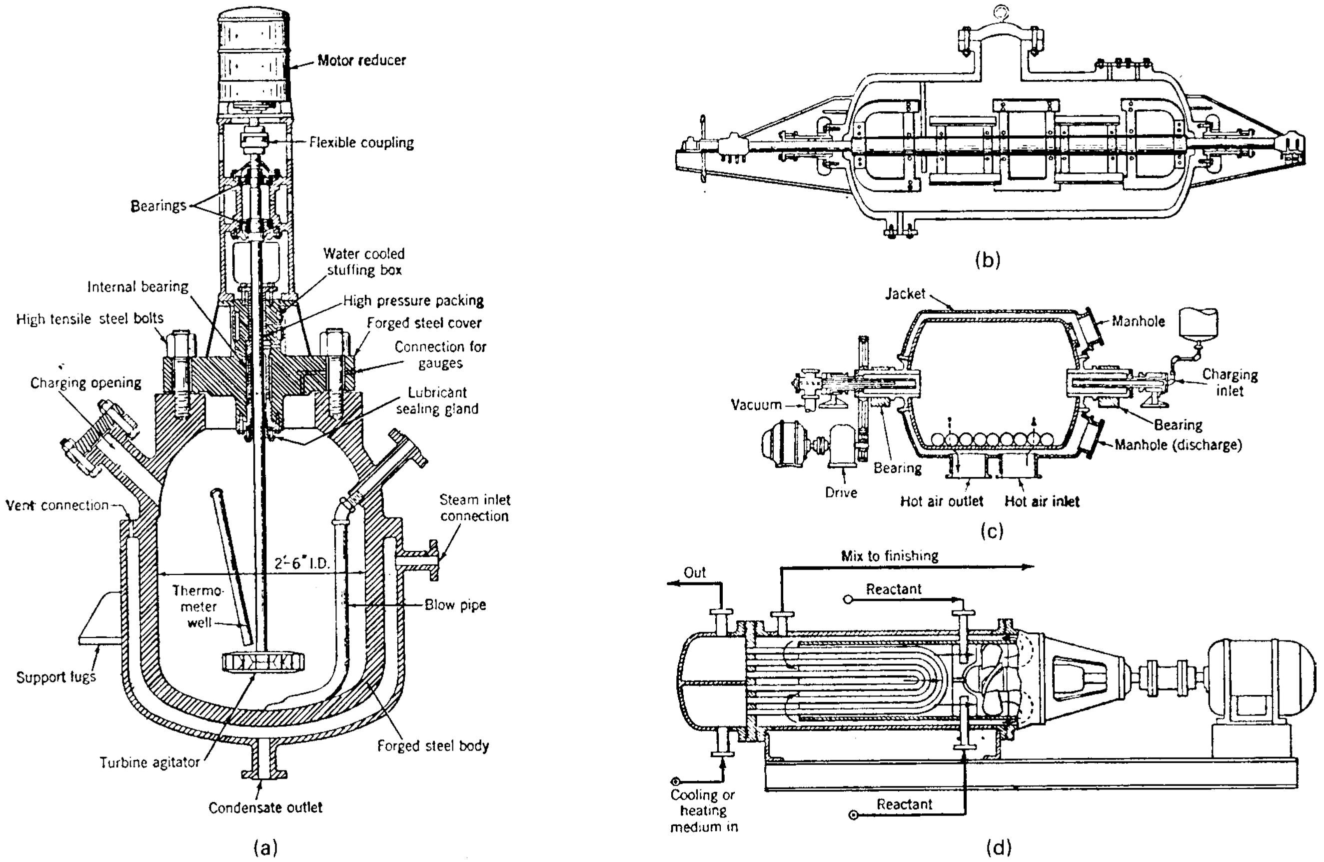


Figure 17.10. Several modes of mixing in commercial tank reactors. (a) Steam-jacketed autoclave, 120 gal, 200 psig, 300°F (*courtesy Blaw-Knox Co.*). (b) Horizontal autoclave, 650 gal, 100 psig (*courtesy Blaw-Knox Co.*). (c) Ball-mill sulfonator [*Groggins. Courtesy McGraw-Hill, New York*]. (d) Horizontal heat-exchange reactor (*courtesy Stratford Engineering Corp. patents issued,* Walas, 1988).

valid if the residence time is 5–10 times the mixing time, which is the length of time needed to achieve homogeneity of a mixture of several inputs. Therefore, the CISTR is used as a preliminary model to simplify the engineering calculations.

Often this is achieved by 50–200 revolutions of a properly designed stirrer. Although mixing times have been the subject of many studies in the literature (Westerterp et al., 1984, p. 254) (see Table 17.1), no useful generalizations have been deduced. The mixing time depends on the geometry and the speed and power of the agitator. A propeller above and a turbine below on the same shaft, baffles attached to the wall of the tank, and possibly a draft tube around the shaft for effective recirculation of the contents constitute a basic design. However, rational design of mixing equipment is possible but in critical cases experts should be consulted. Chapter 10 also deals with this topic.

Power input per unit volume and impeller tip speeds are often used measures of the intensity of stirring, assuming correct proportions of the vessel and proper baffling. Appropriate ranges for some reaction conditions are as tabulated:

Operation	kW/m^3[a]	Tip speed (m/sec)
Blending	0.05–0.1	
Homogeneous reaction	0.1–0.3	2.5–3.3
Reaction with heat transfer	0.3–1.0	3.5–5.0
Gas-liquid, liquid-liquid	1–2	5–6
Slurries	2–5	

[a] $1\ kW/m^3 = 5.08\ HP/1000\ gal$.

Heat transfer coefficients in stirred tank operations are discussed in Section 17.7.

For a given load and conversion, the total volume of a CSTR (continuous stirred tank reactor) battery decreases with the number of stages, sharply at first and then more slowly. When the reaction is first order, for example, $r = kC$, the ratio of total reactor volume V_r of n stages to the volumetric feed rate V_0' is represented by

$$kV_r/V_0' = n[(C_0/C)1/n - 1] \tag{17.33}$$

At conversions of 95 and 99%, some values from this equation are

n	1	2	3	4	5	10
kV_r/V_0' at 95%	19	6.9	5.1	4.5	5.1	3.5
kV_r/V_0' at 99%	99	18.0	10.9	9.7	7.6	5.9

Since the cost of additional controls, agitators, and pumps can counterbalance the savings in volume, four or five tanks in a battery normally prove to be an optimum number, but a larger number of stages may be economical with a single shell design like Figure 17.9(d), particularly when the stages are much less efficient than ideal ones.

For some purposes it is adequate to assume that a battery of five or so CSTRs is a close enough approximation to a plug flow reactor. The tubular flow reactor is smaller and cheaper than any comparable tank battery, even a single shell arrangement. For a

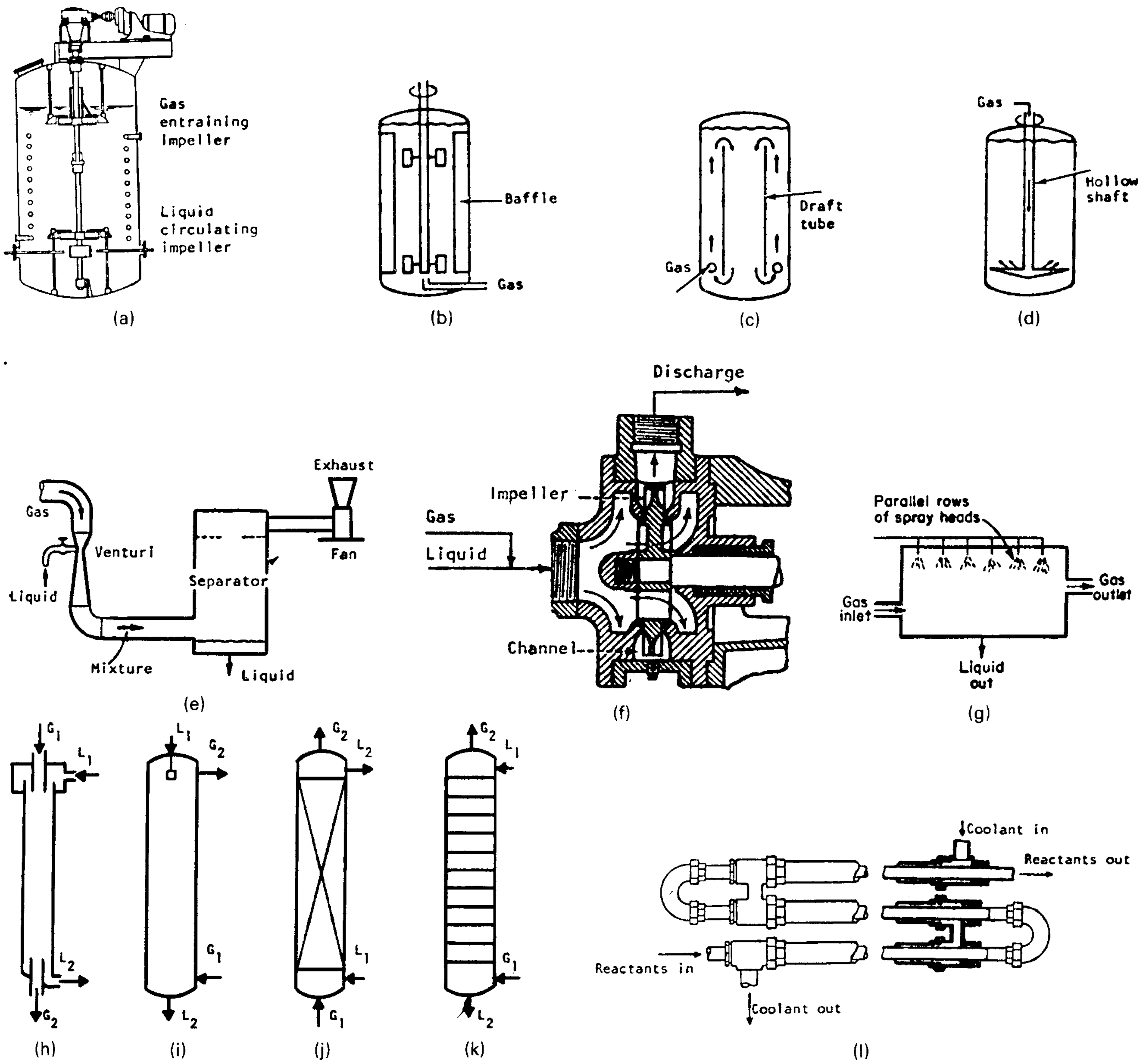


Figure 17.11. Types of contactors for reacting gases with liquids; many of these also are suitable for reacting immiscible liquids. Tanks: (a) with a gas entraining impeller; (b) with baffled impellers; (c) with a draft tube; (d) with gas input through a rotating hollow shaft. (e) Venturi mixer for rapid reactions. (f) Self-priming turbine pump as a mixer-reactor. (g) Multispray chamber. Towers: (h) parallel flow falling film; (i) spray tower with gas as continuous phase; (j) parallel flow packed tower; (k) counter flow tray tower. (l) A doublepipe heat exchanger used as a tubular reactor.

first-order reaction the ratio of volumes of an n-stage CSTR and a PFR is represented by

$$(V_r)_{\mathrm{CSTR}}/(V_r)_{\mathrm{PFR}} = n[(C_0/C)^{1/n} - 1]/\ln(C_0/C). \qquad (17.34)$$

For example, when $n = 5$ and conversion is 99%, the ratio is 1.64. For second-order and other-order reactions a numerical solution for the ratio is needed, one of which is represented by Figure 17.12. For a second-order reaction the ratio is 1.51 at 99% conversion with five stages.

A further difference between CSTR batteries and PFRs is that of product distributions with complex reactions. In the simple case, $A \rightarrow B \rightarrow C$ for example, a higher yield of intermediate product B is obtained in a PFR than in a single CSTR. It is not possible to generalize the results completely, so that the algebra of each individual reacting system must be solved to find the best mode.

TUBULAR PLUG FLOW REACTORS

The ideal behavior of tubular flow reactors (TFR) is plug flow, in which all nonreacting molecules have equal residence times. This

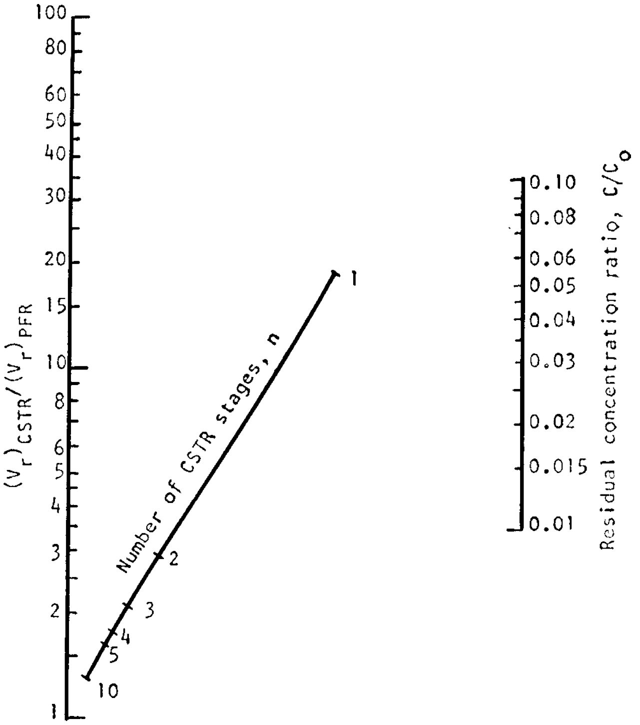


Figure 17.12. Ratio of volumes of an *n*-stage CSTR battery and a plug flow reactor as a function of residual concentration ratio C/C_0 with a rate equation $r = kC^2$.

type reactor is essentially a tube or pipe through which one or more fluids are pumped. As the fluids are pumped through the reactor, the chemical reaction proceeds, creating a gradient with respect to the distance traveled. At the reactor entrance, the reaction rate is very high but as the concentration of the reactants decrease, the product concentration increases. In the design of a PFR, it is assumed that there is no upstream or downstream mixing, i.e. plug flow. Reactants may be introduced into the reactor at various locations other than the inlet and a higher efficiency is obtained, hence the size and cost of the reactor is reduced. A PFR has a higher efficiency than a CSTR of the same volume and with a given space-time, a reaction will proceed to a higher percentage completion in a PFR than in a CSTR.

Any backmixing that occurs is incidental, the result of natural turbulence or that induced by obstructions to flow by catalyst granules or tower packing or necessary internals of the vessels. The action of such obstructions can be two-edged, however, in that some local backmixing may occur, but on the whole a good approach to plug flow is developed because large scale turbulence is inhibited. Any required initial blending of reactants is accomplished in mixing nozzles or by in-line mixers discussed in Section 10.11, Chapter 10. Commercial in-line mixer components are shown in Figure 10.20. As a result of chemical reaction, gradients of concentration and temperature are developed in the axial direction of TFRs.

TFRs may be of pipe diameters ranging from 1 to 15 cm or so, or they may be vessels of diameters measured in meters. Figure 17.13 is of a variety of vessel configurations. Single tube reactors more than 1000 m long are used, in which case they are trombone-shaped as on Figures 17.14(f) and 17.15(c). The selection of diameter is a result of compromise between construction cost, pumping cost, and required heat transfer. In some cases it may be necessary to avoid the laminar flow region, which is below Reynolds numbers of 2300–4000 or so, if the reaction is complex and a spread of residence times is harmful.

When many tubes in parallel are needed, a shell-and-tube construction like that of heat exchangers is employed; the vessel then may be regarded as a heat exchanger in which a reaction occurs incidentally. Heat transfer to single tubes is accomplished with jackets in Figure 17.14(f) and in a fired heater in Figure 17.15(c). Some of the many designs of fired heaters that are suitable for pyrolysis and other high temperature reactions are illustrated on Figure 17.16. In the process for making phenol, monochlorbenzene, and aqueous caustic are reacted at 320°C and 200 atm in multipass tubes of 10 cm dia or so in a fired heater.

In general, the construction of TFRs is dictated by the need for accommodation of granular catalysts as well as for heat transfer. Some of the many possible arrangements are illustrated on Figure 17.13 and elsewhere in this section.

Some unusual flow reactors are shown in Figure 17.14. The residence times in the units for high temperature pyrolysis to make acetylene and ethylene and for the oxidation of ammonia are measured in fractions of a second; acetic anhydride is made by mixing reactants quickly in a centrifugal pump; NO is formed at very high temperature in an electric furnace; and ethylene is polymerized at high or low pressures in the two units shown.

GAS–LIQUID REACTIONS

Except with highly volatile liquids, reactions between gases and liquids occur in the liquid phase, following a transfer of gaseous participants through gas and liquid films. The rate of mass transfer always is a major or limiting factor in the overall transformation process. Naturally the equipment for such reactions is similar to that for the absorption of chemically inert gases, namely towers and stirred tanks. Figure 17.11 illustrates schematically types of gas-liquid reactors. Figure 17.17 shows specific examples of such reactors: In the synthesis of butynediol, acetylene at high pressure is bubbled into aqueous formaldehyde at several positions along a tower in (a). The heat of absorption of nitrogen oxides in water to make nitric acid is removed in two ways in the equipment of (b) and (e). Fats are hydrogenated in a continuous multistage stirred reactor in (c) and under batch conditions in a coil-cooled stirred tank in (d). A thin film reactor is used for the sulfonation of dodecylbenzene with SO_3 in (f). Hydrogen is recirculated with a hollow-shaft agitator to convert nitrocaprolactam in (g). A shell-and-tube design is used for the reaction of ammonia and adipic acid in (h).

Reactions between gases and liquids may involve solids also, either as reactants or as catalysts. Table 17.9 lists a number of examples. The lime/limestone slurry process is the predominant one for removal of SO_2 from power plant flue gases. In this case it is known that the rate of the reaction is controlled by the rate of mass transfer through the gas film.

Some gases present in waste gases are recovered by scrubbing with absorbent chemicals that form loose compounds; the absorbent then may be recovered for reuse by elevating the temperature or lowering the pressure in a regenerator. Such loose compounds may exert appreciable back pressure in the absorber, which must be taken into account when that equipment is to be sized.

In all cases, a limiting reactor size may be found on the basis of mass transfer coefficients and zero back pressure, but a size determined this way may be too large in some cases to be economically acceptable. Design procedures for mass transfer equipment are in other chapters of this book. Data for the design of gas-liquid reactors or chemical absorbers may be found in books such as those by Astarita et al. (1983) and Kohl and Nielsen (1979).

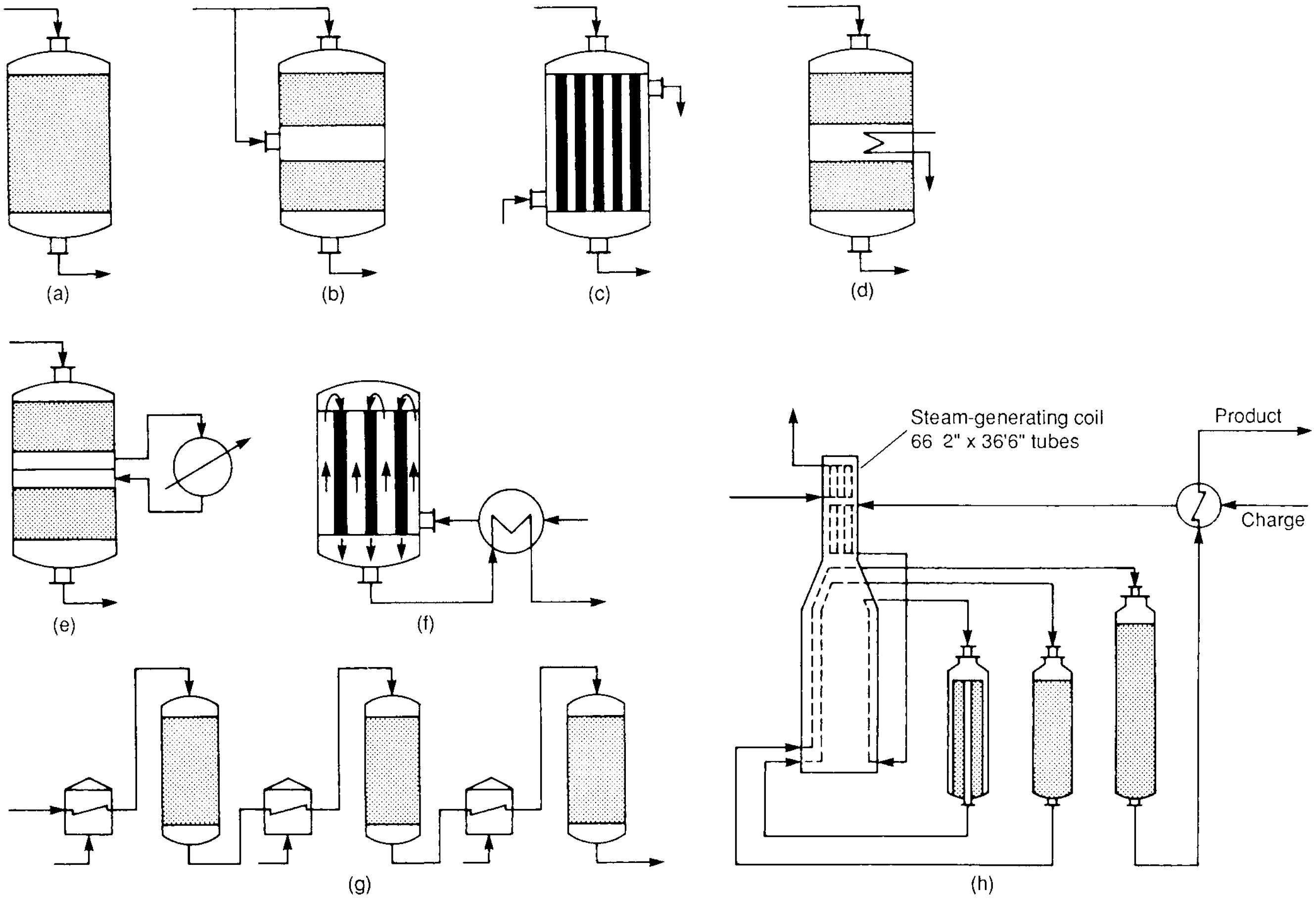


Figure 17.13. Multibed catalytic reactors (a) adiabatic; (b) interbed coldshot injection; (c) shell and tube; (d) built-in interbed heat exchanger; (e) external interbed exchanger; (f) autothermal shell, outside influent-effluent heat exchanger; (g) multishell adiabatic reactor with interstage fired heaters; (h) platinum-catalyst, fixed bed reformer for 5000 bpsd charge rate; reactors 1 and 2 are 5.5 ft dia by 9.5 ft high and reactor 3 is 6.5 × 12.0 ft. (Walas, 1988).

GAS-SOLID REACTIONS

Fixed Bed Reactors

The fixed beds of concern here are made up of catalyst particles in the range of 2–5 mm dia. Vessels that contain inert solids with the sole purpose of improving mass transfer between phases and developing plug flow behavior are not in this category. Other uses of inert packings are for purposes of heat transfer, as in pebble heaters and induction heated granular beds—these also are covered elsewhere.

The catalyst in a reactor may be loaded in several ways, as:

1. a single large bed,
2. several horizontal beds,
3. several packed tubes in a single shell,
4. a single bed with imbedded tubes,
5. beds in separate shells.

Some of the possibilities are illustrated in Figures 17.13 and 17.18. Variations from a single large bed are primarily because of a need for control of temperature by appropriate heat transfer, but also for redistribution of the flow or for control of pressure drop. There are few fixed bed units that do not have some provision for heat transfer. Only when the heat of reaction is small is it possible to regulate the inlet temperature so as to make adiabatic operation feasible; butane dehydrogenation, for example, is done this way.

Koch has developed and designed a fixed-bed reactor which increased the mean residence time (MRT) by as much as 60% through the installation of a unique feed gas distribution. The Koch reactors are large in diameter and shallow in height. To distribute the entering gases across the catalyst bed, an elliptical head diffuser is installed inside the reactor near the entering nozzle. It consists of 3 to 5 concentric cones that are interconnected by structural elements. Inlet gases strike an inlet plate and are evenly distributed to the various passages. The pressure drop throughout the device is about 0.5 psi. (Chem. Eng., 2001). Although this partially solves the distribution problem, other problems such as lost catalyst activity, catalyst fluidization and hot spots are only partially reduced. (Chem. Eng., 2001).

Because of their long industrial histories and worldwide practice, the sulfuric acid and ammonia industries have been particularly inventive with regard to reactors. A few designs for SO_2 oxidation are illustrated in Figure 17.19. Their dominant differences are in modes of temperature control to take advantage of high rates of reaction at high temperature and favorable equilibrium conversion at lower temperatures. Figure 17.19(g) shows the temperature profile achieved in that equipment.

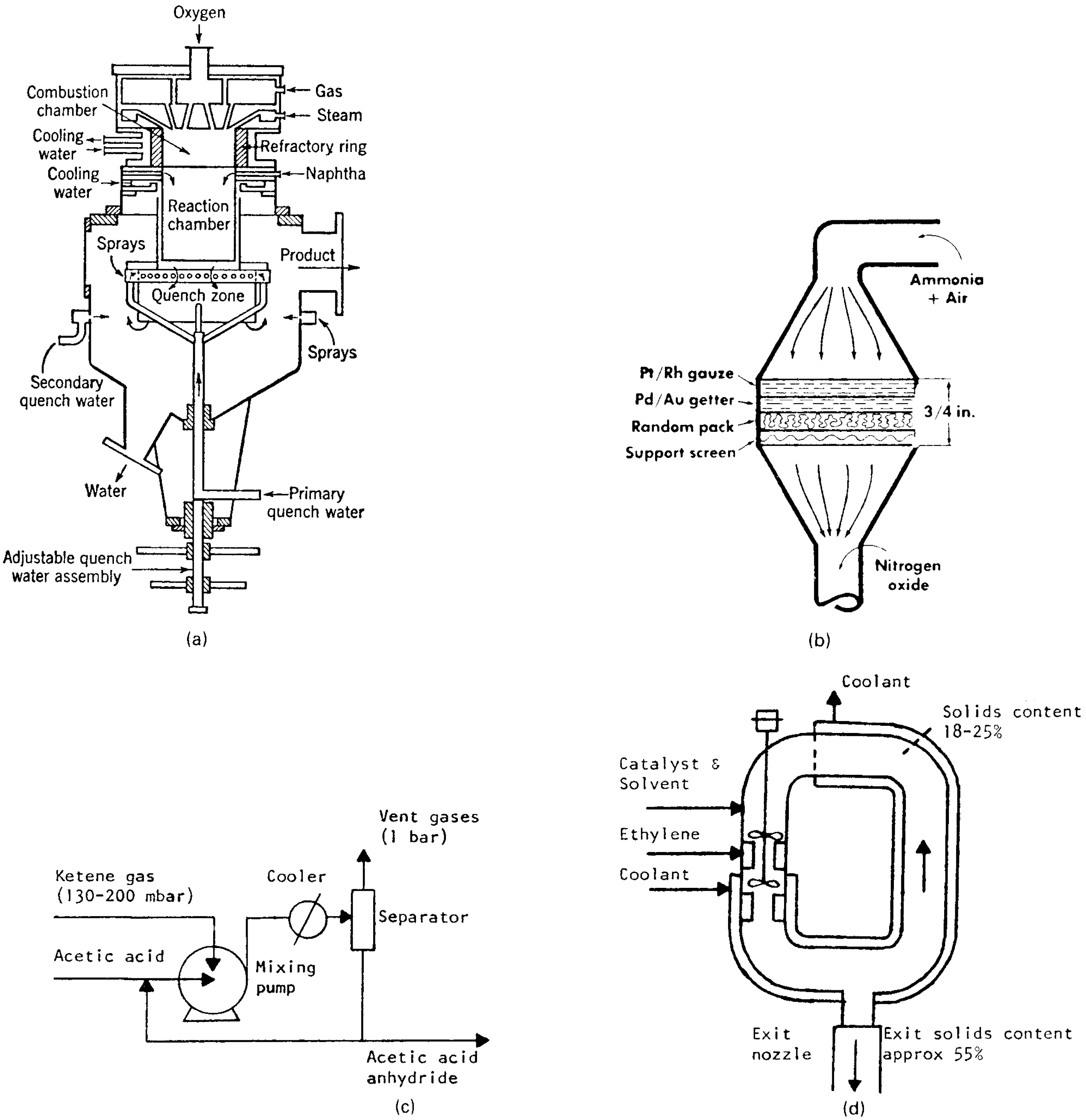


Figure 17.14. Some unusual reactor configurations. (a) Flame reactor for making ethylene and acetylene from liquid hydrocarbons (*Patton et al., 1958*). (b) Shallow bed reactor for oxidation of ammonia, using Pt-Rh gauze (*Gillespie and Kenson, Oct. 1971*). (c) Production of acetic acid anhydride from acetic acid and gaseous ketene in a mixing pump. (d) Phillips reactor for low pressure polymerization of ethylene (closed loop tubular reactor). (e) Polymerization of ethylene at high pressure.

In Figure 17.20, patterns of temperature control in multibed reactors for the manufacture of SO_2, ammonia and methanol are presented.

A selection of classic ammonia reactors and their elaborate means for temperature regulation are illustrated in Figures 17.21 and 17.22 showing the development of such reactors. There have been some modifications and updates of these reactors. Included is an autothermal ammonia reactor, a radial-flow converter and a horizontal three-bed converter. In Figure 17.21 of this third edition, a more modern high capacity single unit type converter and comparative performance data with various manufacturers is presented. A vessel sketch, typical temperature profile and other data of the ICI quench-type single stage converter is shown. Note that the quench is supplied at two points (ICI).

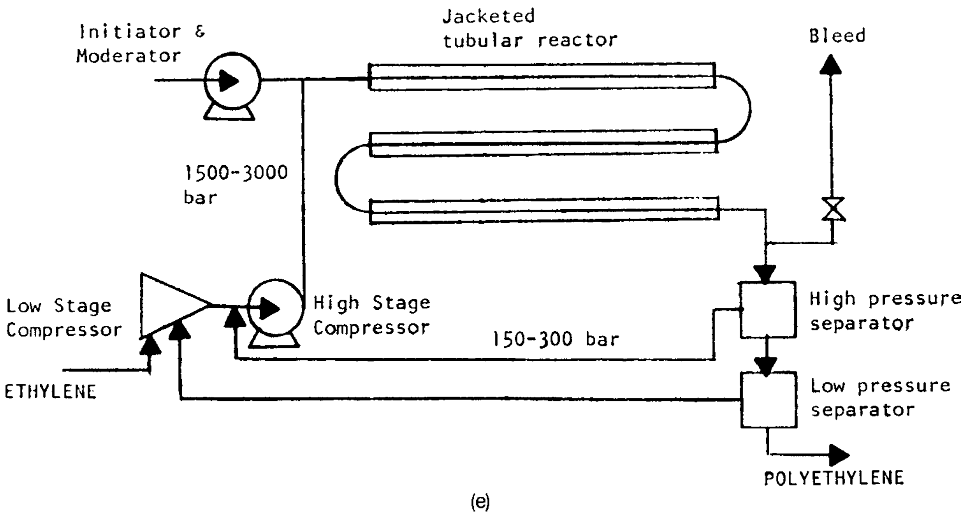


Figure 17.14.—(*continued*)

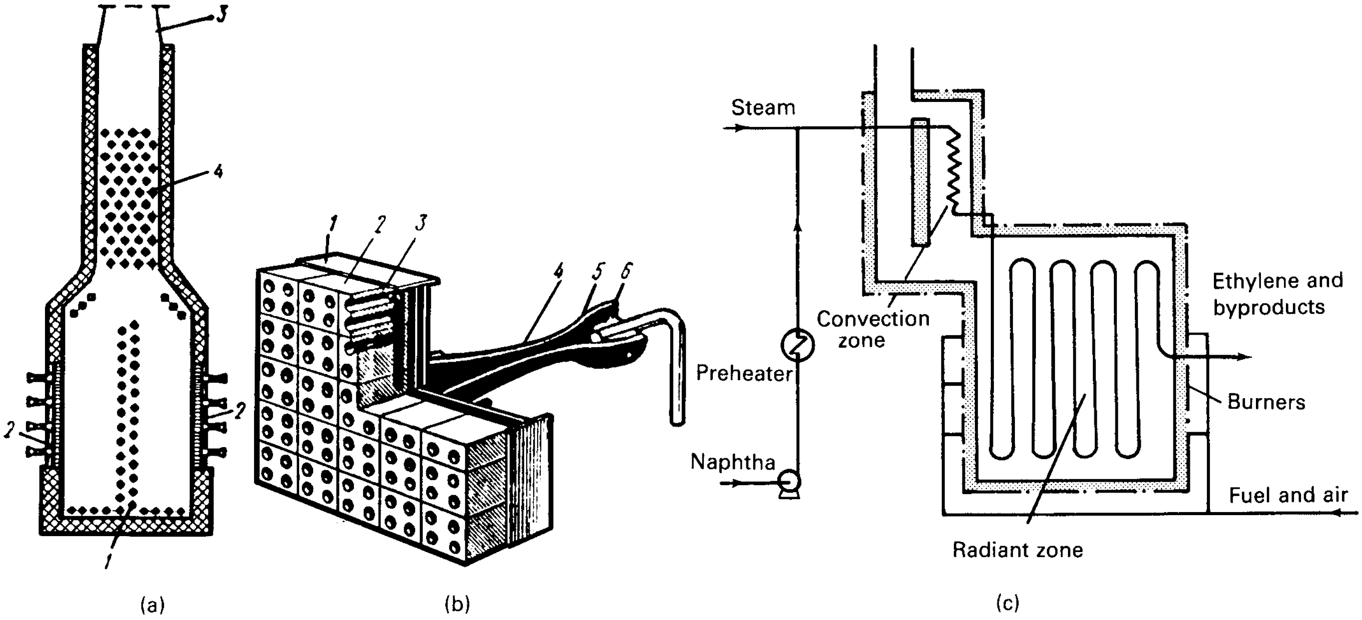


Figure 17.15. A fired heater as a high temperature reactor. (a) Arrangement of tubes and burners: (1) radiant tubes; (2) radiant panel burners; (3) stack; (4) convection chamber tubes (*Sukhanov, 1982*). (b) Radiant (surface-combustion) panel burner: (1) housing; (2) ceramic perforated prism; (3) tube; (4) injector; (5) fuel gas nozzle; (6) air throttle (*Sukhanov, 1982*). (c) Fired tubular cracking furnace for the preparation of ethylene from naphtha. (Walas, 1988).

The most significant improvements to earlier ammonia plant designs have been in the reactor (synthesis) units. Uhde has developed a Dual-Pressure Process that is a medium pressure, once-through synthesis in series with a conventional high pressure synthesis loop. A single converter with three radial type catalyst beds over two reactors while the synthesis loop includes another three radial type catalyst beds over two reactors. This arrangement leads to process improvements like increased yields and increased energy efficiency. KBR has developed a proprietary ammonia reactor design technology using graphite-supported ruthenium catalyst which is reported to have an activity up to 20 times that of conventional iron-magnetite catalysts. In this process, the synthesis loop pressure is lowered to about 90 bars, resulting in reported significant savings in capital costs and maintenance. (Chem. Eng., 2008).

Thermal effects also are major factors in the design of reactors for making synthetic fuels. The units of Figure 17.24 for synthesis of methanol and gasoline are typical fixed bed types.

Catalytic reformers upgrade low octane naphthas into gasoline in the presence of hydrogen to retard deposition of carbon on the catalyst. Temperatures to 500°C and pressures to 35 atm are necessary. Representative reactors are shown in Figure 17.25. Feedstocks to such units usually must be desulfurized; a reactor like that of Figure 17.26 hydrogenates sulfur compounds to hydrogen sulfide, which is readily removed.

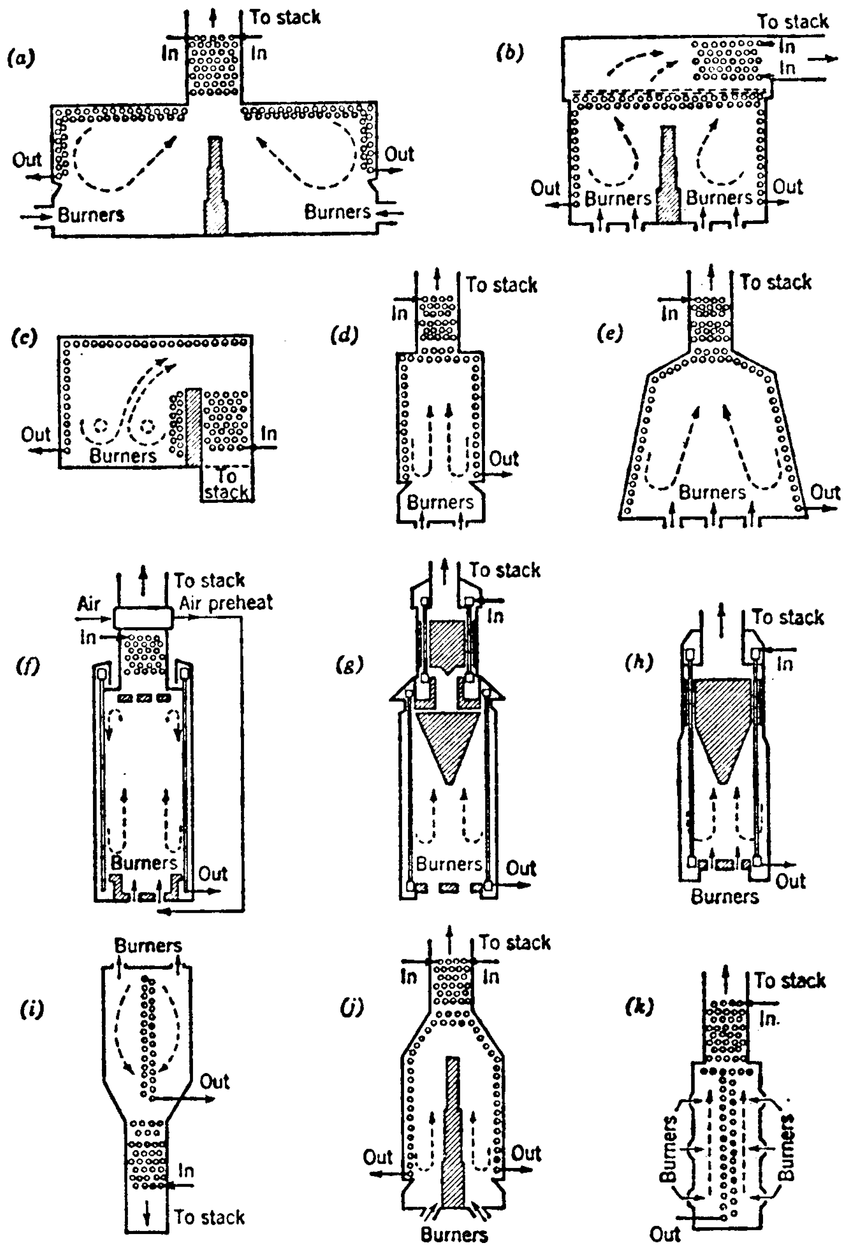


Figure 17.16. Basic types of tubular furnaces (Nelson, 1958. Courtesy McGraw-Hill, New York, Walas, 1988).

Fluid flow through fixed bed reactors usually is downward. Instead of screens for supporting catalyst in the vessel, a support of graduated sizes of inert material is used, as illustrated in Figure 17.27. Screens become blinded by the small particles of catalyst. A similar arrangement is used at the top to prevent disturbance of the catalyst level by the high velocity fluids.

MOVING BEDS

In moving-bed reactors, granular or solid lumps move vertically downward as a mass. The solid may be a reactant, catalyst or heat carrier. In the second edition of this book (Couper et al., 2005) Figure 17.28a, a pebble heater was used for the fixation of nitrogen of nitrogen in air. Similarly, a pebble heater, Figure 17.28(a) of this edition, was suggested for the pyrolysis of oils to make ethylene, however, it was not a competitive process and was abandoned. Units like Figure 17.28(b) were employed in the catalytic cracking of gas oils. The catalyst was transferred between the regenerating and reacting zones with air lifts or bucket elevators. Some data for this equipment are given with this figure.

Two examples in which the solid itself is reactive are the shale oil retorts of Figure 17.29. Crushed oil shale is charged at the top,

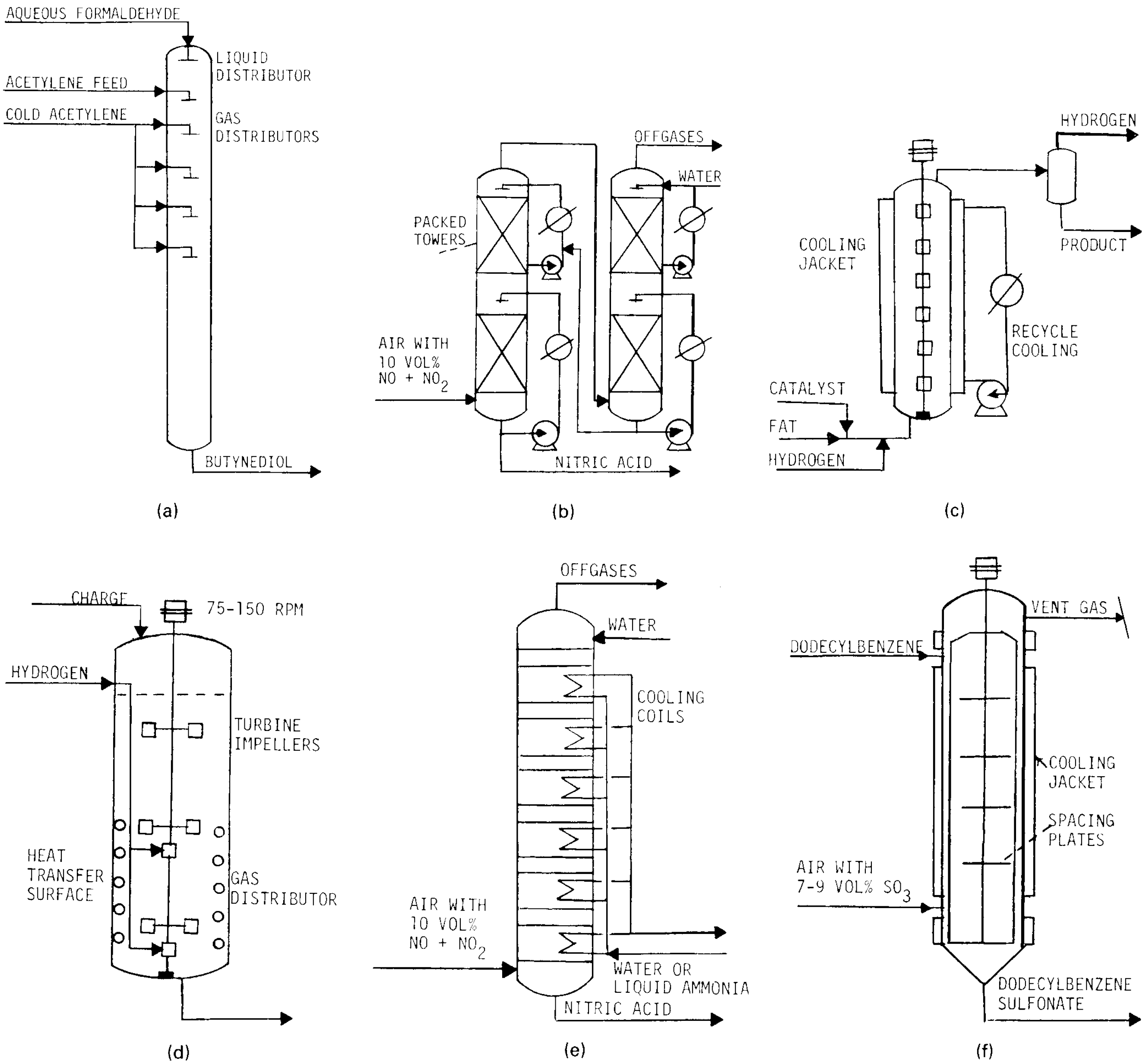


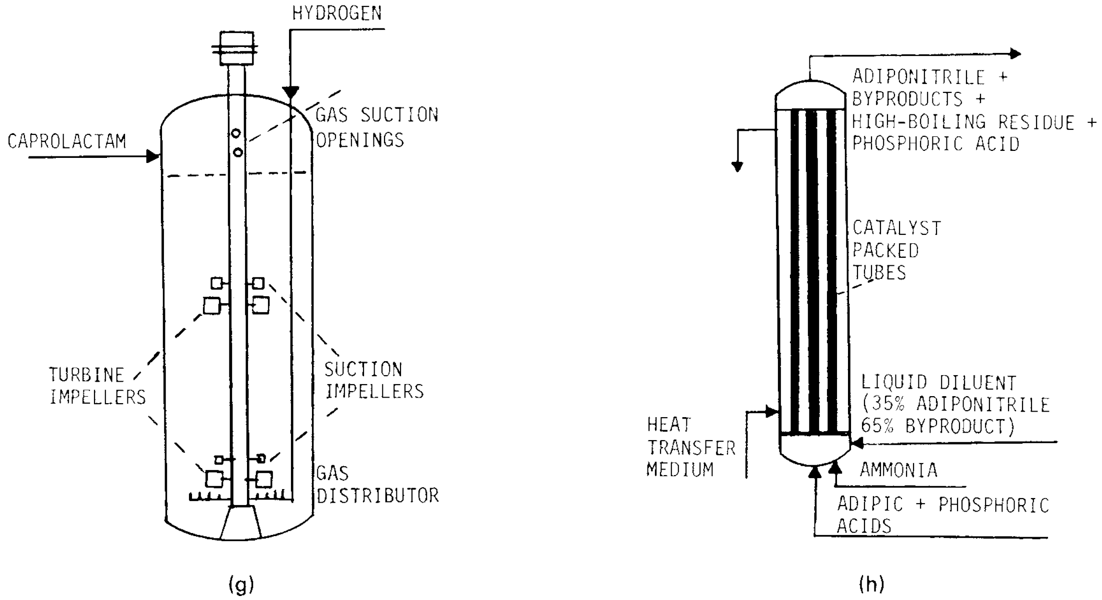
Figure 17.17. Examples of reactors for specific liquid-gas processes. (a) Trickle reactor for synthesis of butynediol 1.5 m dia by 18 m high. (b) Nitrogen oxide absorption in packed columns. (c) Continuous hydrogenation of fats. (d) Stirred tank reactor for batch hydrogenation of fats. (e) Nitrogen oxide absorption in a plate column. (f) A thin film reactor for making dodecylbenzene sulfonate with SO_3. (g) Stirred tank reactor for the hydrogenation of caprolactam. (h) Tubular reactor for making adiponitrile from adipic acid in the presence of phosphoric acid.

air and gaseous fuel at the bottom. When the shale moving downward reaches a temperature of 900°F, the kerogen decomposes into oil vapor, gas, and carbonaceous residue. Figure 17.29(b) was developed for the Paraho Oil Shale demonstration in Colorado.

KILNS AND HEARTH FURNACES

These units are primarily for high temperature services, the kilns up to 2500°F and the furnaces up to 4000°F. Usual construction is steel-lined with ceramics, sometimes up to several feet in thickness. Typical units are shown in Figure 17.30.

Vertical kilns are used for materials that do not fuse or soften, as for the burning of limestone or dolomite. Many such operations are batch: the fresh solid is loaded into the kiln, heated with combustion products until reaction is complete, and then dumped. The lime kiln of Figure 17.30(c), however, operates continuously as a moving bed reactor. These vessels range in size from 8 to 15 ft dia and are 50–80 ft high. For calcination of lime the peak temperatures are about 2200°F, although decomposition proceeds freely at 1850°F. Fuel supply may be coke mixed with the limestone if the finished lime can tolerate the additional ash, or gaseous or liquid fuels. Space velocity is



(g) (h)

Figure 17.17.—(*continued*)

TABLE 17.9. Examples of Fluidized Bed Processes

A. Catalytic Processes

1. Oil cracking and reforming
2. Recovery of high concentrations of benzene from gas oils
3. Olefin production from crude oil
4. Chlorine by oxidation of HCl
5. Acetylene from methane
6. Preparation of unsaturated aldehydes
7. Reduction of nitro compounds to amines
8. Oxidation of SO2 to SO3
9. Phthalic anhydride from naphthalene or o-xylene
10. Maleic acid anhydride from benzene
11. Formaldehyde from methanol
12. Chlorination of methane and ethylene
13. Fischer–Tropsch synthesis of gasoline
14. Hydrogenation of ethylene
15. Oxidation of ammonia
16. Ethylene oxide from ethylene
17. Butadiene from ethanol
18. Dehydrogenation of isopropanol
19. Isomerization of n-butane
20. Post-chlorination of PVC
21. Decomposition of ozone
22. Preparation of chlorinated hydrocarbons
23. Preparation of melamine resins
24. Isoprene synthesis
25. Reduction of vinyl acetate
26. Preparation of acrylonitrile

B. Noncatalytic Processes

1. Gasification of coal
2. Fluid bed coking
3. Pyrolytic cracking of methane
4. Preparation of activated carbon
5. Ethylene by cracking of petroleum fractions
6. Combustion of coal
7. Burning of oil shale
8. Combustion of municipal and industrial wastes
9. Burning of black liquor (paper industry)
10. Roasting of sulfides of iron, copper, and zinc
11. Combustion of sulfur in a sand bed
12. Decomposition of waste sulfuric acid and sulfates
13. Cracking of chlorides such as $FeCl_2$, $NiCl_3$, and $AlCl_3$
14. Volatilization of rhenium
15. Burning of limestone and dolomite
16. Cement burning
17. Reduction of iron ores and metallic oxides
18. Chlorination of ores of aluminum, titanium, nickel, cobalt, and tin
19. Chlorination of roasted pyrites and iron ores
20. Chlorination of lime
21. Calcination of aluminum hydroxide to alumina
22. Preparation of aluminum sulfate from bauxite
23. Preparation of fluorides aluminum trifluoride, uranium tetra- and hexafluorides
24. Preparation of pure tungsten from the fluoride
25. Calcination of phosphates
26. Preparation of phosphorus oxychloride
27. Preparation of carbon disulfide
28. Preparation of hydrazine
29. Preparation of nitric acid
30. Preparation of nitrates of ammonia and sodium
31. Preparation of sodium carbonate
32. Preparation of hydrogen cyanide
33. Hydrochlorination of uranium fuel elements
34. Preparation of uranium trioxide from the nitrate
35. Recovery of uranium from nuclear fuels
36. Removal of fluorine from offgases of aluminum electrolysis
37. Heating of heat transfer media such as sand
38. Cooling of granular masses such as fertilizers
39. Drying of finely divided materials such as flotation ores and raw phosphates
40. Coating of fuel elements by pyrolytic cracking of chlormethylsilanes

(Walas, 1988).

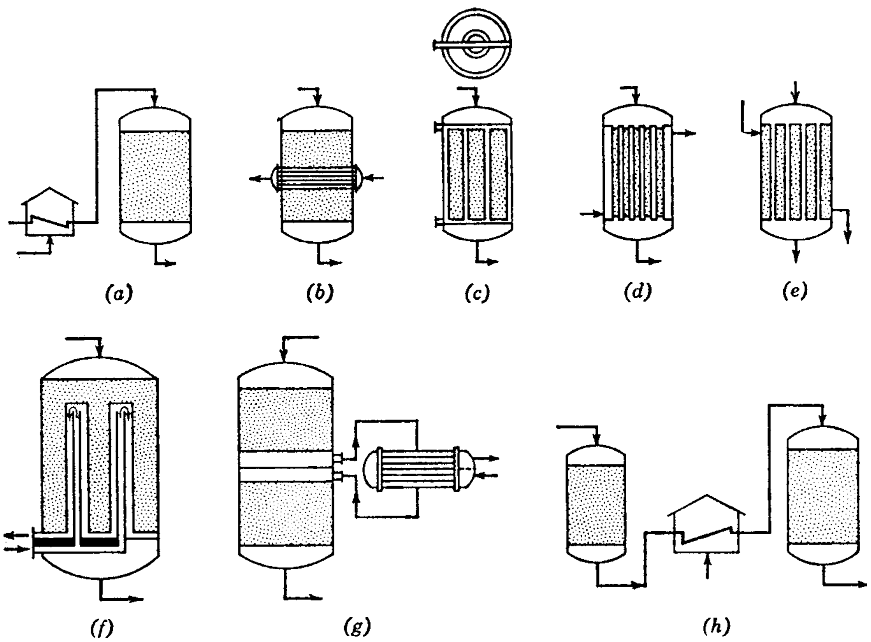


Figure 17.18. Heat transfer in fixed-bed reactors (a) adequate preheat; (b) internal heat exchanger; (c) annular cooling spaces; (d) packed tubes; (e) packed shell; (f) tube and thimble; (g) external heat exchanger; (h) multiple shell, with external heat transfer (Walas, 1988).

0.8–1.5 lb CaO/(hr)(cuft of kiln), or 45–100 lb CaO/(hr)(sqft of kiln cross section), depending on the size and modernity of the kiln, the method of firing, and the lump size which is in the range of 4–10 in.

Rotary kilns have many applications as reactors: between finely divided solids (cement), between liquids and solids (salt cake from salt and sulfuric acid), between gases and solids, and for the decomposition of solids (SO_3 and lime from $CaSO_4$). The kiln is a long narrow cylinder with a length-to-diameter ratio of 10–20. General purpose kilns are 100–125 ft long, but cement kilns as large as 12 ft dia by 425 ft long are operated. An inclination to the horizontal of 2–5 deg is sufficient to move the solid along. Speed of rotation is 0.25–2 rpm. Lumps up to 1 in. dia or fine powders are usual. Heating mostly is with combustion gases, but some low temperature heating may be accomplished through heated jackets. Figures 17.30(a) and (c) show the temperature profiles of gas and stock in a cement kiln and space velocities of a number of kiln processes.

Hearth furnaces consist of one or more flat or concave pans, either moving or stationary, usually equipped with scraper-stirrers. Although such equipment is used mostly for ore treating and metallurgical purposes, a few inorganic chemical processes utilize them, for example, Leblanc soda ash, sodium sulfide from salt cake and coal, sodium sulfate and hydrogen chloride from salt and sulfuric acid, and sodium silicate from sand and soda ash.

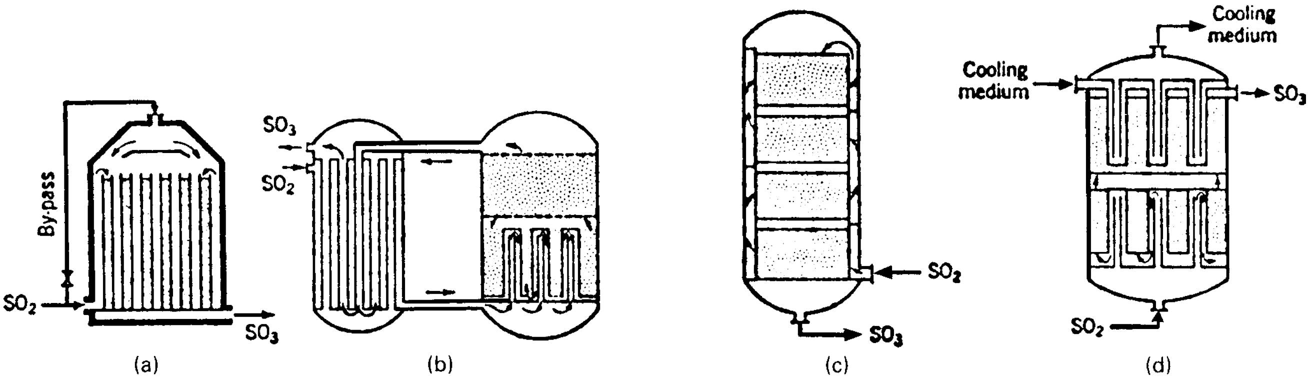
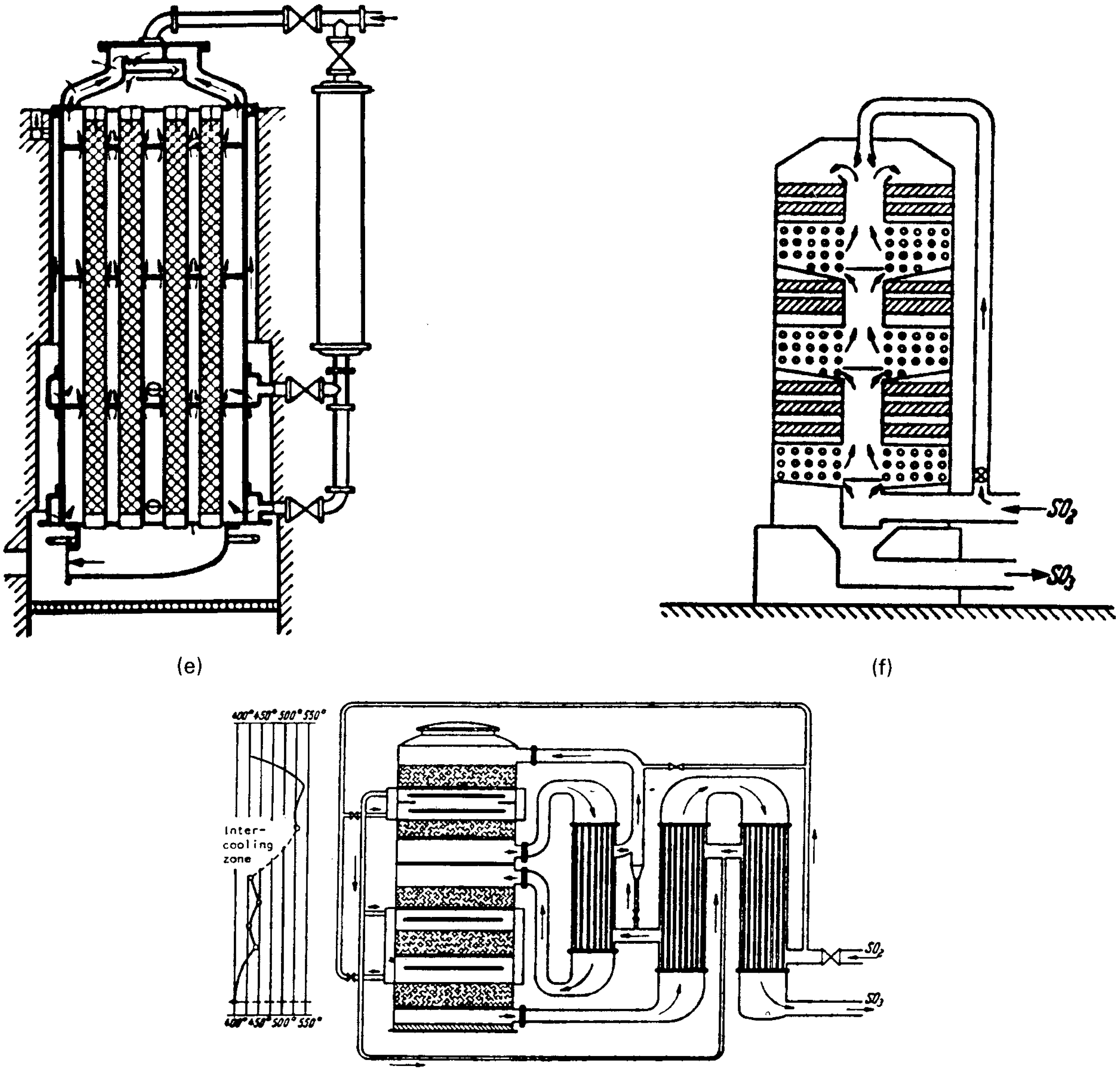


Figure 17.19. Reactors for the oxidation of sulfur dioxide: (a) Feed-product heat exchange. (b) External heat exchanger and internal tube and thimble. (c) Multibed reactor, cooling with charge gas in a spiral jacket. (d) Tube and thimble for feed against product and for heat transfer medium. (e) BASF-Knietsch, with autothermal packed tubes and external exchanger. (f) Sper reactor with internal heat transfer surface. (g) Zieren-Chemiebau reactor assembly and the temperature profile (Winnacker-Weingartner, 1950–1954).



(e)

(f)

(g)

Figure 17.19.—(*continued*)

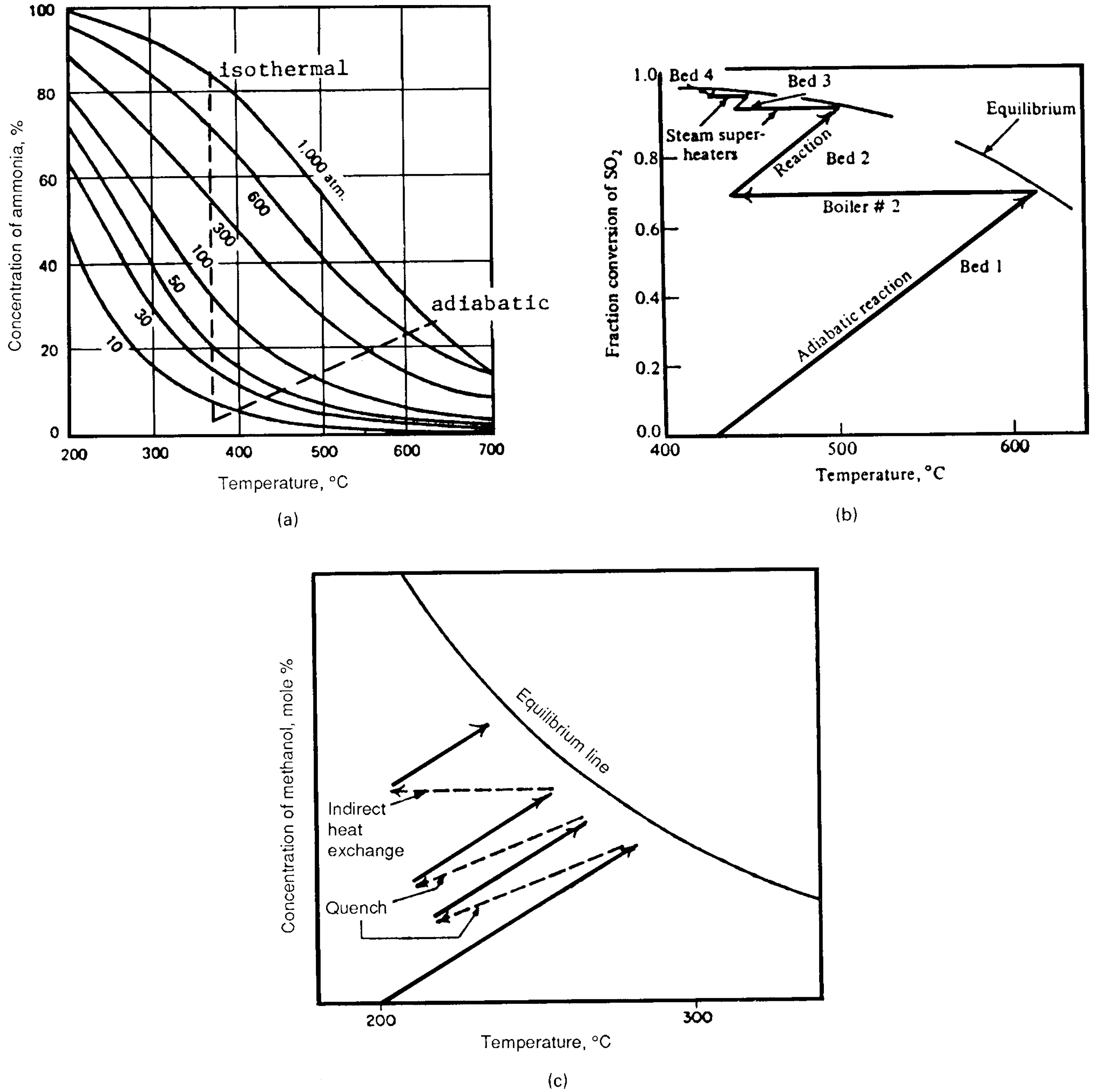
Examples of these units were shown in Figures 17.30d and f of the previous edition of this book. (Couper et al., 2005). Very high temperature operations like the manufacturing of glass or metals utilize single-hearth furnaces equipped with heat regenerators for fuel economy.

Multiple-hearth furnaces are suited to continuous handling of solids that exhibit a limited amount of fusion or sintering. In the kind shown on Figure 17.30(d), the scrapers rotate, in other kinds the plates rotate, and in still others the scrapers oscillate and discharge the plates at each stroke. Material is charged at the top, moves along as rotation proceeds, and drops onto successively lower plates while combustion gases or gaseous reactants flow upward. This equipment is used to roast ores, burn calcium sulfate or bauxite, and reactivate the absorbent clays of the petroleum industry. A reactor with nine trays, 16 ft dia and 35 ft high can roast about 1,250 lb/hr of iron pyrite, at a residence time of about 4–5 hr.

FLUIDIZED BED REACTORS

This term is restricted here to equipment in which finely divided solids in suspension interact with gases. Solids fluidized by liquids are called slurries. Three phase fluidized mixtures occur in some coal liquefaction and petroleum treating processes. In dense phase gas-solid fluidization, a fairly definite bed level is maintained; in dilute phase systems the solid is entrained continuously through the reaction zone and is separated out in a subsequent zone.

The most extensive application of fluidization has been to catalytic cracking of petroleum fractions. Because the catalyst degrades in a few minutes, it is circulated continuously between



(a)

(b)

(c)

Figure 17.20. Control of temperature in multibed reactors so as to utilize the high rates of reaction at high temperatures and the more favorable equilibrium conversion at lower temperatures. (a) Adiabatic and isothermal reaction lines on the equilibrium diagram for ammonia synthesis. (b) Oxidation of SO_2 in a four-bed reactor at essentially atmospheric pressure. (c) Methanol synthesis in a four bed reactor by the ICI process at 50 atm; not to scale; 35% methanol at 250°C, 8.2% at 300°C, equilibrium concentrations. (Walas, 1988).

reaction and regeneration zones. Figure 17.31(a) is a version of such equipment, although there have been some updated versions. The steam stripper is for the removal of occluded oil before the catalyst is to be burned. The main control instrumentation of a side-by-side system is shown in Figure 3.19 h (Walas, 1988).

Fluid catalytic vessels are very large. Dimensions and performance of a medium capacity unit (about 50,000 BPSD, 60 kg/sec) are shown with the figure. Other data for a reactor to handle 15,000 BPSD are a diameter of 25 ft and a height of 50 ft. Catalyst holdup and other data of such a reactor are given by Kraft et al. (in Othmer, 1956) as follows:

Item	Quantity
Unit charge, nominal	15,000 BPSD
Catalyst inventory, total	250 tons
Catalyst inventory, regenerator bed	100 tons
Superficial velocity, regenerator	2.5 fps
Bed density, regenerator	28.0 lb/cuft
Flue gas plus solids density, cyclone inlet	0.5 lb/cuft
Catalyst circulation rate, unit	24.0 tons/min
Catalyst circulation rate, to cyclones	7.0 tons/min
Catalyst loss rate, design expectation	2.0 tons/day

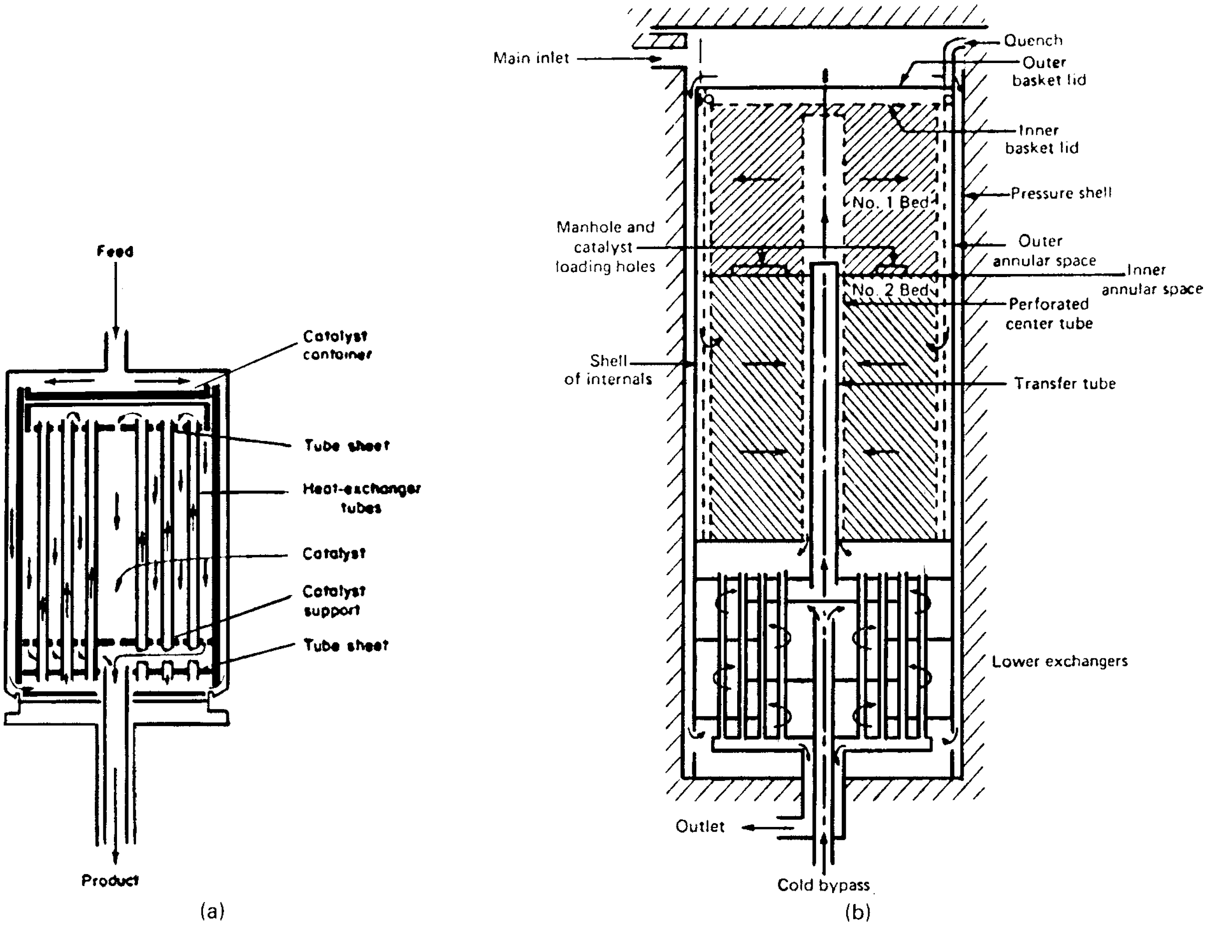


Figure 17.21. Some designs of ammonia synthesis converters. (a) Principle of the autothermal ammonia synthesis reactor. Flow is downwards along the wall to keep it cool, up through tubes imbedded in the catalyst, down through the catalyst, through the effluent-influent exchanger and out. (b) Radial flow converter with capacities to 1800 tons/day (Haldor Topsoe Co., Hellerup, Denmark, Walas, 1988).

Figure 17.31(b) is of a unit in which most of the cracking occurs in a transfer line, an operation that became feasible with the development of highly active zeolite catalysts. The reaction is completed in the upper zone, but the main function of that zone is to separate product and spent catalyst. In contrast to the dense-phase bed of a large reactor, in which mixing can approach ideality, the dilute phase transfer line is more nearly in plug flow. Accordingly, a much smaller reaction zone suffices; moreover, superior product distribution and greater gasoline yield result. Similar reactor configurations are shown in Figures 17.31(c) and (d) of other petroleum processes.

The mechanism of interaction between catalyst and gas in a large fluidized bed is complex and is not well correlated with design factors. In the bed itself, large bubbles of a foot or more in diameter form and are irrigated with a rain of catalyst particles. This process occurs in parallel with a well-mixed fluidized bed. Above the bed level and before the entrained catalyst is recovered in cyclones, the reaction continues in dilute phase plug flow. Since even the physical behavior of fluidized beds is not well understood, the design of such reactors is done largely on the basis of fairly large pilot plants and by analogy with earlier experience in this area.

The earliest fluidized process was the noncatalytic Winkler process for gasification of coal in 1921. Other noncatalytic processes, and some catalytic ones, are listed in Table 17.9. A few noncatalytic reactors are shown in Figure 17.32. Cracking of naphthas to ethylene with circulating hot sand as the heat carrier is shown in part (a); at the operating temperature of 720–850°C, much carbon deposits on the sand but is not at all harmful as it would be on the surfaces of tubular cracking units. In the dilute phase process of calcination of alumina, part (b), the circulating solid is the product itself; combustion products from sprays of oil and auxiliary air furnish the motive power. The calcining unit for lime of part (c) is an example of a successful multistage reactor; residence time in the calcining zone is 2 hr, in the cooling zone 0.5 hr, and in each of the preheating zones 1 hr. Multibed units for petroleum operations have not been feasible, but some units have been built with a degree of baffling that simulates staging in a rough fashion. The catalyst of the phthalic anhydride reactor of part (d) does not need to be regenerated so the fluidized bed remains in place; since the reaction is highly sensitive to temperature, the oxidation is kept under control with much imbedded heat transfer surface and by cold injections. A typical coal gasifier appears in part (e); a thirty-fold circulation of spent char is employed along with the fresh feed to counteract the agglomeration tendency of many coals. The H-Coal reactor of part (f) operates with a three-phase mixture. The catalyst does not circulate but bubbles in place. Activity is maintained by bleeding off and replenishing 1–2% of the catalyst holdup per day. Operating conditions are 450°C and 3000 psig. Both coal and heavy petroleum residua are handled successfully. The unit is known as an "ebullating bed."

The literature of fluidization phenomena and technology is extensive. A good although dated bibliography is in *Ullmann's Encyclopedia* (1973, Vol. 3, pp. 458–460). The book by Cheremisinoff and Cheremisinoff (1984) has more than 500 abstracts of articles on fluidization hydrodynamics, mixing and heat transfer, but little on reactor technology. Other literature on fluidization is cited in the References of Chapter 6.

17.7. HEAT TRANSFER IN REACTORS

Maintenance of proper temperature is a major aspect of reactor operation. The illustrations of several reactors in this chapter depict a number of provisions for heat transfer. The magnitude of required heat transfer is determined by heat and material balances as described in Section 17.3. The data needed are thermal conductivities and coefficients of heat transfer. Some of the factors influencing these quantities are associated in the usual groups for heat transfer; namely, the Nusselt, Stanton, Prandtl, and Reynolds dimensionless groups. Other characteristics of particular kinds of reactors also are brought into correlations. A selection of practical results from the abundant literature is assembled here. Some modes of heat transfer to stirred and fixed bed reactors are represented in Figures 17.33 and 17.18, and temperature profiles in several industrial reactors appear in Figures 17.21, 17.23, 17.30, 17.34, and 17.35.

STIRRED TANKS

Values of overall coefficients of heat transfer are collected in Tables 17.10–17.12. Two sets of formulas for tank-side film coefficients are in Tables 17.13 and 17.14. They relate the Nusselt number to the Reynolds and Prandtl numbers and several other factors. In the equation for jacketed tanks, for example,

$$h_0(\text{jacket})\frac{T}{k} = 0.85\left(\frac{D^2N\rho}{\mu}\right)^{0.66}\left(\frac{C_p\mu}{k}\right)^{0.33}\left(\frac{\mu}{\mu_s}\right)^{0.14}\times\left(\frac{Z}{T}\right)^{-0.56}\left(\frac{D}{T}\right)^{0.13} \tag{17.35}$$

the rpm, the tank and impeller diameters, and the liquid depth as well as a viscosity ratio are involved. Table 17.14 identifies the kind of impeller that was used in the investigation, but in general test results have shown that approximately the same heat transfer coefficient is obtained with flat-blade turbines, pitched-blade turbines, or propellers. Axial flow turbines produce the most circulation for a given power input and heat transfer is related directly to the flow, so that this kind of impeller usually is favored. From Eq. (17.35), the coefficient is proportional to the 0.66 power of the rpm, $N^{0.66}$, and from Chapter 10, the power input at high Reynolds numbers varies as the cube root of N. Accordingly it appears that the coefficient is proportional to the 0.22 exponent of the power input to the stirred tank,

$$h \propto P^{0.22}$$

and consequently that the coefficient of heat transfer is little affected by large increases of power input.

Batch reactors have been designed and controlled by essentially the same method over the past 5 decades with minor modifications. Temperature control in large reactors has been troublesome because they respond slowly to heat load changes and may even have the potential for localized temperature changes and hot spots and thus give erratic temperature control. Batch reactors must have good temperature control and monitoring of a process. In general, they are slow to respond to heat load changes and may even have potential for localized temperature changes and hot spots and result in erratic temperature control. Innovations in jacket design, such as versatile heat transfer surface permits the user to regulate the jacket area and jacket temperature in real time. Two conventional designs have been used in industry, the fully jacketed vessel, Figure 17.9(e) and the half-coil jacket vessel, Figure 17.9(f). The latter unit has multiple heat transfer channels and permits the regulation of heat transfer surface. This results in heating or cooling without changing the jacket heat transfer fluid, providing a constant heat flux. Hot or cold spots disappear and the amount of heat transferred can be altered without changing the jacket temperatures. Effectively, the jacket acts as a split jacket. In both simulated and line tests, the constant heat flux jacket permits more stable and faster control characteristics compared to conventional jacketed vessels (Ashe et al., 2008).

Most of the literature in the stirred tank category is dated, but since there is little new material of significance, practicing engineers apparently believe what is available is adequate or perhaps has been kept confidential. Table 17.14 contains the recommended equations.

The safety of batch reactions was discussed by Kurasny (2008) with special emphasis on good temperature control. He prepared a safety checklist for designers.

PACKED BED THERMAL CONDUCTIVITY

The presence of particles makes the effective conductivity of a gas greater than the molecular conductivity by a factor of 10 or more. The nature of the solid has little effect at Reynolds numbers above 100 or so; although the effect is noticeable at the lower values of Re, it has not been completely studied. Besides the Reynolds, Prandtl, and Peclet numbers, the effective diffusivity depends on

Typical Data for ICI Quench Converters of Various Sizes

Capacity (short tpd)	660	990	1100	1650
Pressure (psig)	4700	3200	4250	3220
Inlet gas composition (%)				
Ammonia	4.0	3.0	3.2	1.4
Inerts	15.0	12.0	15.0	12.0
Inlet gas flow (MM scfh)	10.6	18.0	18.5	24.5
Catalyst volume (ft^3)	740	1170	1100	2400
Pressure vessel				
Internal diameter (in.)	80	96	95	109
Length (in.)	437	493	472	700
Weight (short ton)				
Cartridge shell	14.2	34.2	22.8	56.4
Heat exchanger	15.5	30.0	25.4	23.8
Pressure vessel (less cover)	130	128	182	240

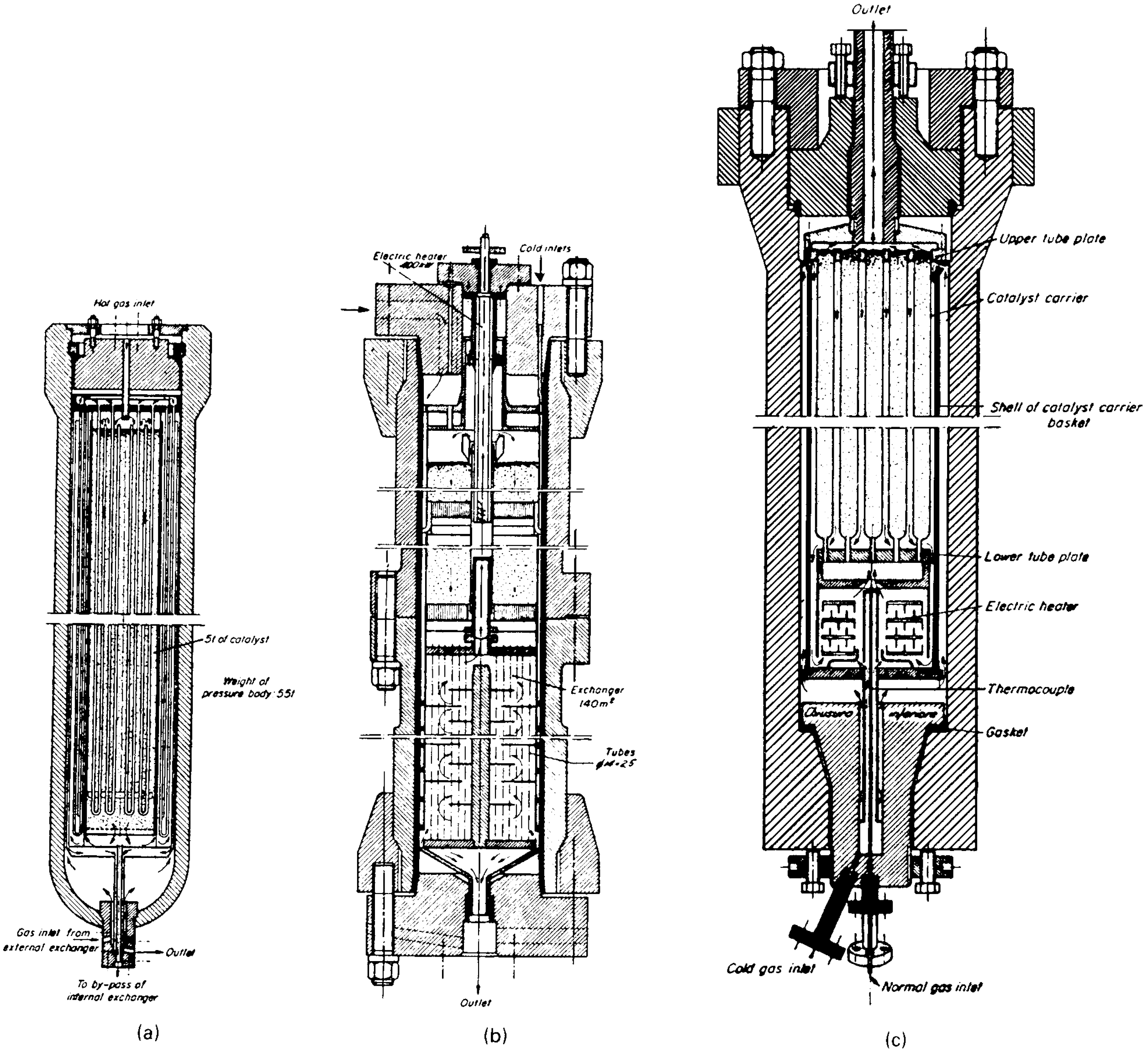
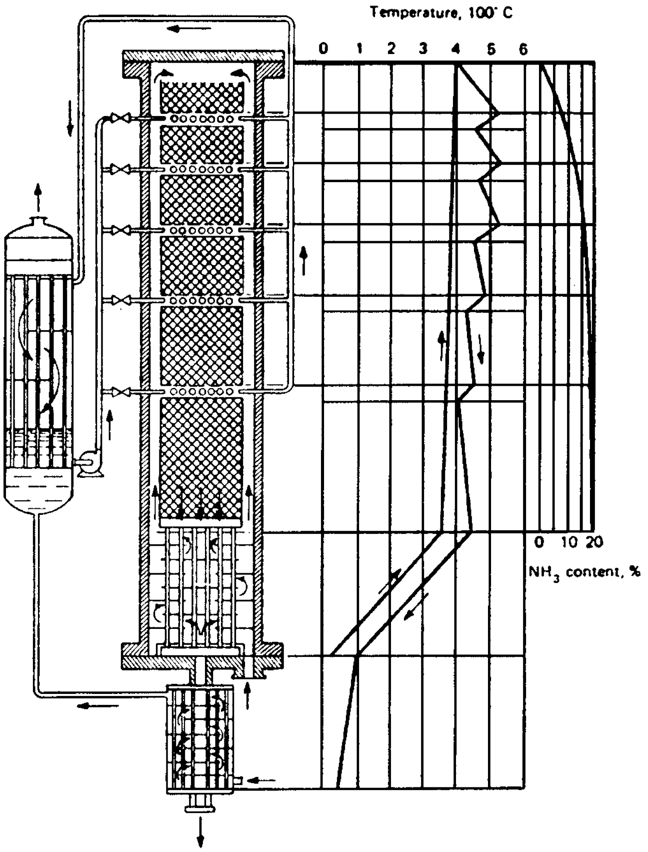


Figure 17.22. Representative ammonia converters operating at various pressures and effluent concentrations. (Vancini, 1971; Walas, 1988). (a) Original Uhde design operating at 125 atm; typical dimensions, 1.4 × 7 m. (b) Haber-Bosch-Mittasch converter operating at 300 atm; typical dimensions, 1.1 × 12.8 m. (c) Claude converter operating at 1000 atm; typical dimensions 1.2 × 7 m. (d) Fauser-Montecatini (old style) converter operating at 300 atm with external heat exchange, showing axial profiles of temperature and ammonia concentration.

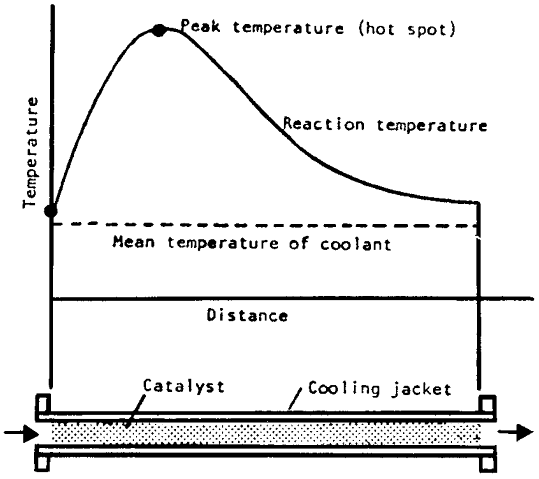
Comparison of Performance

Process	Pressure (bar)	Effluent ammonia (%)	TPD/m^3	Catalyst life (yr)
Uhde	125	7–8	10	>2
Haber-Bosch	300	13–15	25	2
Claude	1000	22–24	120	0.25
Fauser	300	12–17	25	2

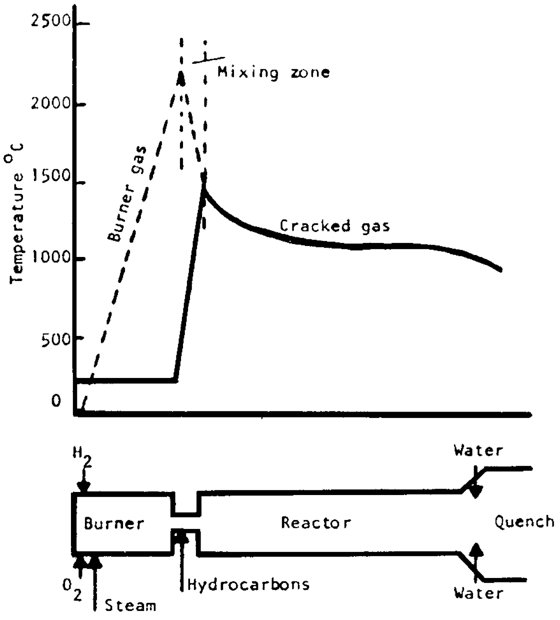


(d)

Figure 17.22.—(*continued*)



(a)



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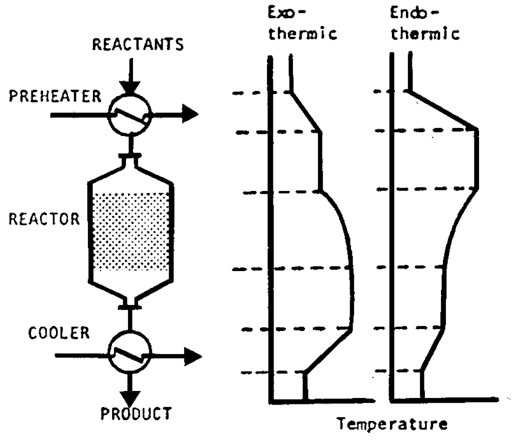
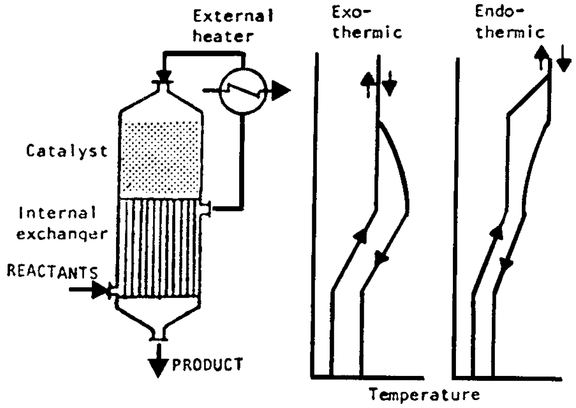
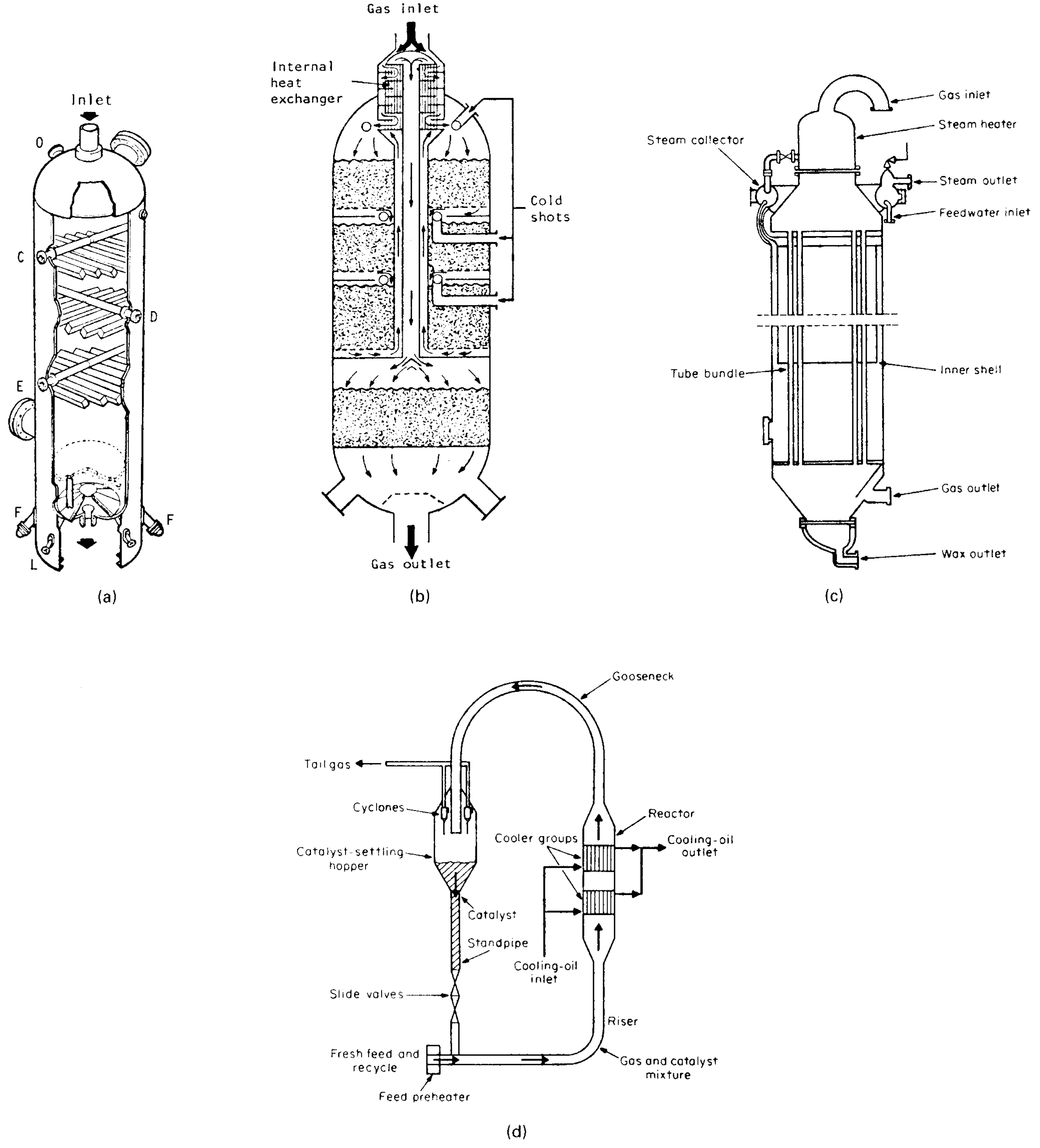


(c)



(d)

Figure 17.23. Representative temperature profiles in reaction systems (see also Figs. 17.20, 17.21(d), 17.22(d), 17.30(c), 17.34, and 17.35). (a) A jacketed tubular reactor. (b) Burner and reactor for high temperature pyrolysis of hydrocarbons (*Ullman, 1973, Vol. 3, p. 355*); (c) A catalytic reactor system in which the feed is preheated to starting temperature and product is properly adjusted; exo- and endothermic profiles. (d) Reactor with built-in heat exchange between feed and product and with external temperature adjustment; exo- and endothermic profiles. (Walas, 1988).



(a) (b) (c)

(d)

Figure 17.24. Types of reactors for synthetic fuels. (Meyers, 1984; Walas, 1988). (a) ICI methanol reactor, showing internal distributors. C, D and E are cold shot nozzles, F = catalyst dropout, L = thermocouple, and O = catalyst input. (b) ICI methanol reactor with internal heat exchange and cold shots. (c) Fixed bed reactor for gasoline from coal synthesis gas; dimensions 10 × 42 ft, 2000 2-in. dia tubes packed with promoted iron catalyst, production rate 5 tons/day per reactor. (d) Synthol fluidized bed continuous reactor system for gasoline from coal synthesis gas.

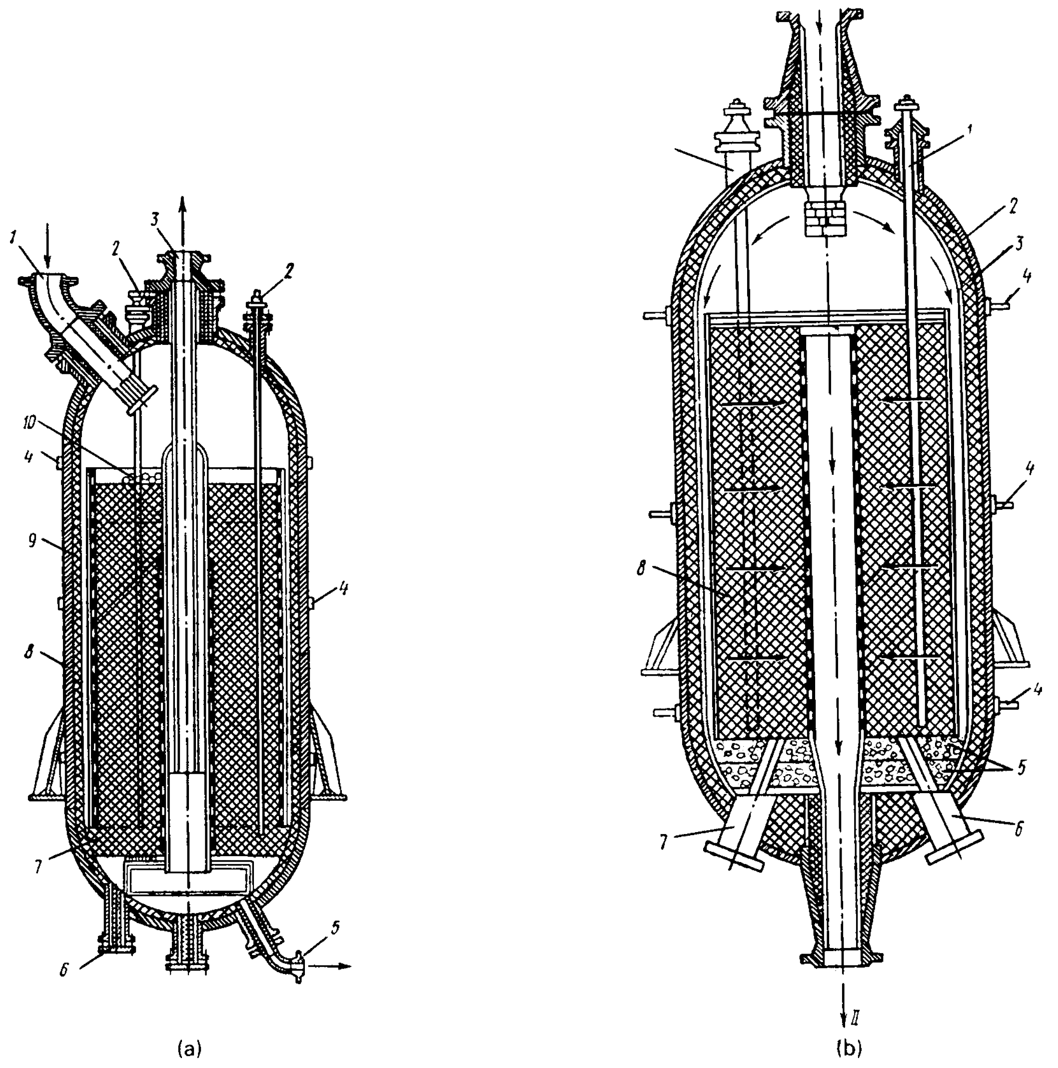


Figure 17.25. Catalytic reforming reactors of axial and radial flow types. The latter is favored because of lower pressure drop (*Sukhanov, 1982; Walas, 1988*). (a) Axial flow pattern. (b) Radial flow pattern.

Typical Data for an ICI Quench Converter of 1300 Short Tons/Day Capacity

Pressure (psig)	2200	3200	4000	4700
Inlet gas flow (MM scfh)[a]	25.8	21.2	19.8	19.0
Catalyst volume (ft^3)	2600	1730	1320	1030
Pressure vessel				
Internal diameter (in.)	120	102	96	89
Length (in.)	663	606	528	488
Weight (short ton)				
Cartridge shell	68.5	40.8	29.2	23.6
Heat exchanger	37.1	25.4	20.7	17.9
Pressure vessel (less cover)	186	184	187	189
Converter pressure drop (psi)	140	104	87	91

[a] Composition: 2% NH_3, 12% inerts (CH_4 + A), 21.5% N_2, 64.5% H_2 by vol.

the molecular conductivity, porosity, particle size, and flow conditions. Plots in terms of Re, Pr, and Pe (without showing actual data points) are made by Beek (1962, Fig. 3), but the simpler plots obtained by a number of investigators in terms of the Reynolds number alone appear on Figure 17.36(a). As Table 17.15 shows, most of the data were obtained with air whose Pr = 0.72 and k_f = 0.026 kcal/(m)(hr)(°C) at about 100°C. Accordingly, the data could be generalized to present the ratio of effective and molecular conductivities as

$$k_e/k_f = 38.5k_e. \qquad (17.36)$$

Equations of the highest and lowest lines on this figure then may be written

$$k_e/k_f = 8.08 + 0.1027\text{Re} \quad \text{(Kwong and Smith)}, \qquad (17.37)$$

$$k_e/k_f = 13.85 + 0.0623\text{Re} \quad \text{(Quinton and Storrow)}. \qquad (17.38)$$

At higher temperatures, above 300°C or so, radiation must contribute to the effective conductivity, but there are so many other uncertainties that the radiation effect has not been studied at length.

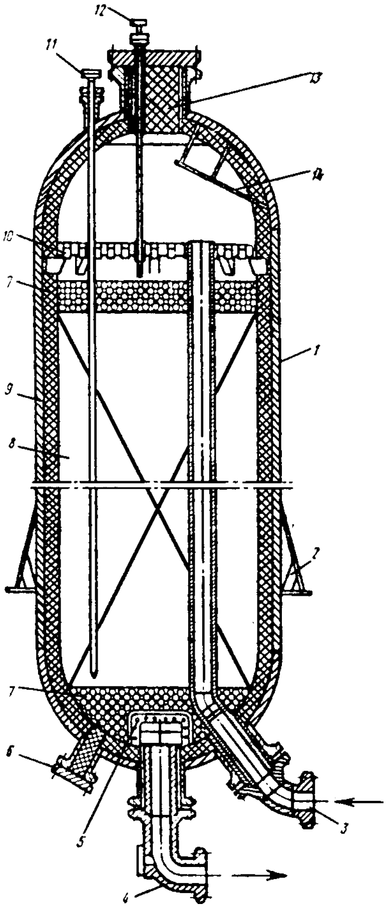


Figure 17.26. Reactor for hydrofining diesel oils, with ceramic lining (Sukhanov, 1982; Walas, 1988).

HEAT TRANSFER AT WALLS, TO PARTICLES, AND OVERALL

The correlations cited in Tables 17.16 and 17.18 are of the Nusselt number in terms of the Reynolds and Prandtl numbers, or of the Reynolds alone. They are applicable only above specified Reynolds numbers, about 40 in most cases; clearly they do not predict correctly the coefficient of natural convection, at $\mathrm{Re} = 0$.

Wall coefficients are obtainable from particle-fluid data by a rule of Beek (1962),

$$h_w = 0.8h_p. \tag{17.39}$$

This is how Eq. (8) of Table 17.18 is deduced; Eq. (9) represents the same data but is simply a curve fit of Figure 17.36(c) at an average value $\mathrm{Pr} = 0.65$.

Data of heat transfer between particle and fluid usually are not measured directly because of the experimental difficulties, but are deduced from measurements of mass transfer coefficients assuming the Colburn analogy to apply,

$$\begin{aligned}(\text{Sherwood})(\text{Schmidt})^{2/3} &= (\text{Nusselt})(\text{Prandtl})^{2/3}\\ &= \text{function of Reynolds.}\end{aligned} \tag{17.40}$$

Thus, in Figure 17.36(c), if the Nusselt number is replaced by the Sherwood and the Prandtl by the Schmidt, the relation will be equally valid for mass transfer.

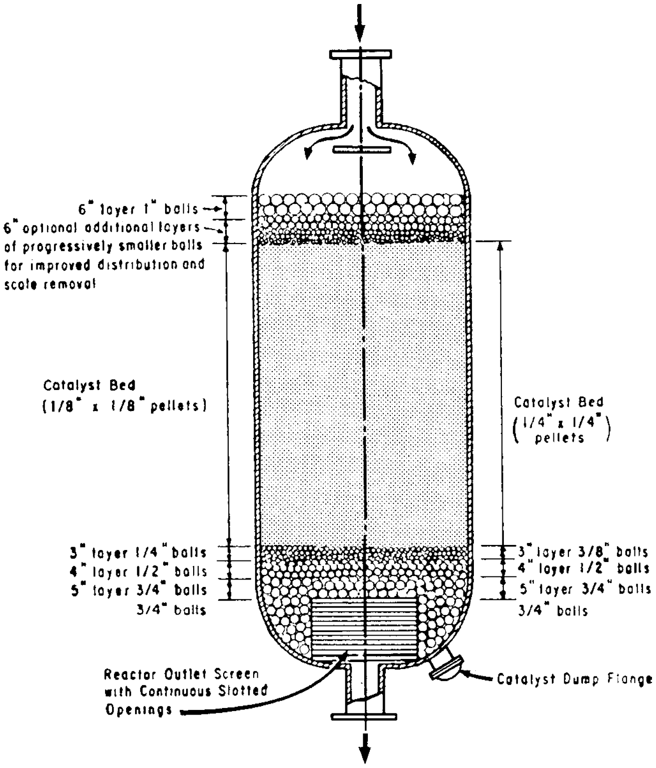


Figure 17.27. Catalyst packed adiabatic reactor, showing application of ceramic balls of graduated sizes for support at the bottom and hold-down at the top. (Rase, 1977).

The ratio, L/D, of length to diameter of a packed tube or vessel has been found to affect the coefficient of heat transfer. This is a dispersion phenomenon in which the Peclet number, uL/D_{disp}, is involved, where D_{disp} is the dispersion coefficient. Some 5000 data points were examined by Schlünder (1978) from this point of view; although the effect of L/D is quite pronounced, no clear pattern was deduced. Industrial reactors have L/D above 50 or so; Eqs. (6) and (7) of Table 17.18 are asymptotic values of the heat transfer coefficient for such situations. They are plotted in Figure 17.36(b).

Most practitioners have been content with correlations of the Nusselt with the Reynolds and Prandtl numbers, or with the Reynolds number alone. The range of numerical values of the Prandtl number of gases is small, and most of the investigations have been conducted with air whose $\mathrm{Pr} = 0.72$ at 100°C. The effect of Pr is small on Figure 17.36(c), and is ignored on Figure 17.36(b) and in some of the equations of Tables 17.17 and 17.18.

The equations of Table 17.18 are the ones recommended for coefficients of heat transfer between wall and fluid in packed vessels.

For design of equipment like those of Figure 17.28, coefficients of heat transfer between particle and fluid should be known. Direct measurements with this objective have been made with metallic packings heated by electrical induction or current. Some correlations are given in Table 17.17. Glaser and Thodos (1958) correlated such data with the equation

$$(h_p/C_pG)(C_p\mu/k)^{2/3} = \frac{0.535}{(\mathrm{Re}')^{0.3} - 1.6}, \quad 100 < \mathrm{Re}' < 9200, \tag{17.41}$$

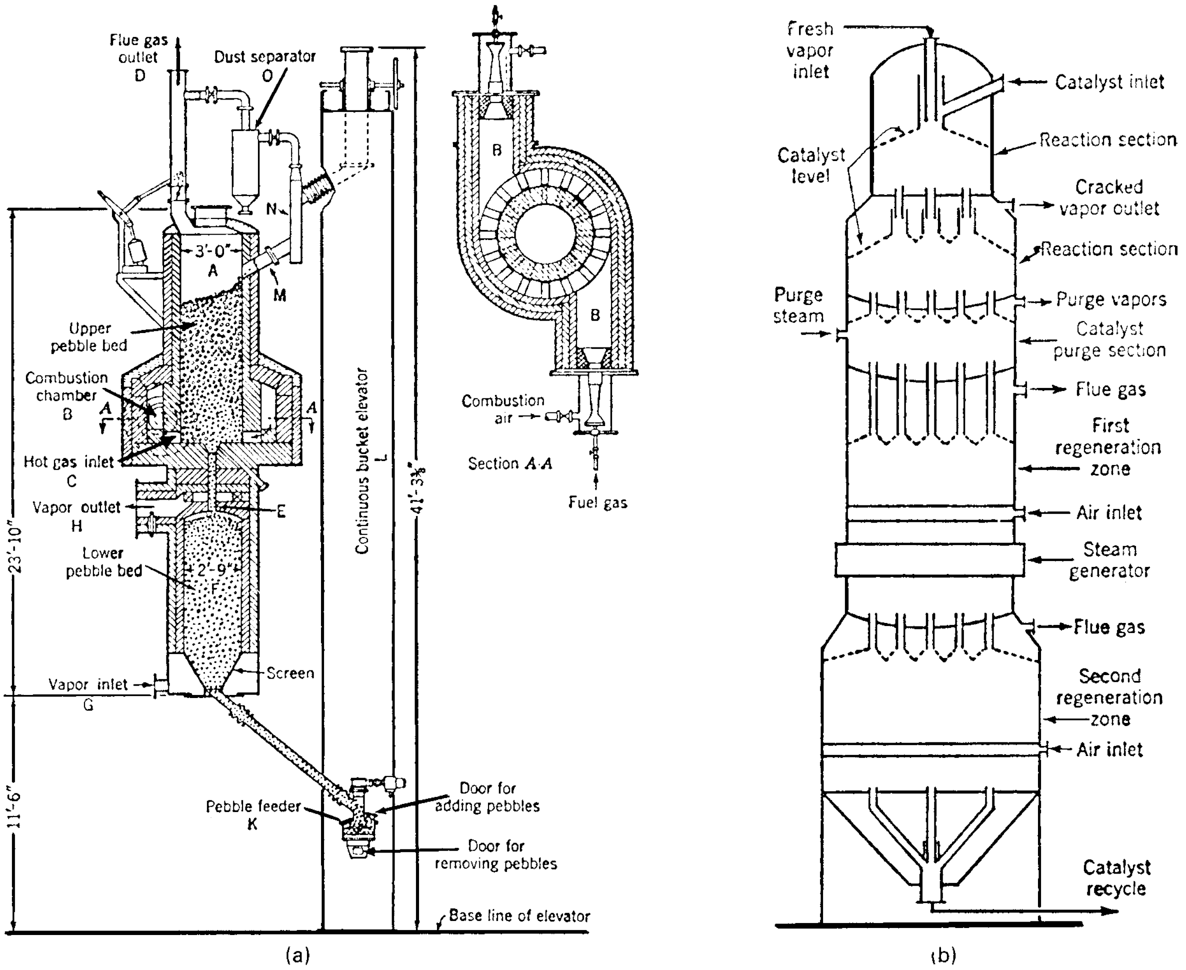


Figure 17.28. Reactors with moving beds of catalyst or solids for heat supply. (a) Pebble heater which has been used for making ethylene from heavier hydrocarbons (*Batchelder and Ingols, 1951*). (b) A typical moving bed catalytic cracker and regenerator; for 20,000 bpsd the reactor is 16 ft dia, catalyst circulation rate 2–7 lbs/lb oil, attrition rate of catalyst 0.1–0.5 lb/ton circulated, pressure drop across air lift line is about 2 psi (*Berg, in Othmer, 1956*). (Walas, 1988).

where

$Re' = \phi\sqrt{a_p}G/\mu(1-\varepsilon)$,
a_p = surface of a single particle,
ϕ = sphericity of the particle.

It has been found that the equations of Table 17.18 also could be used by taking $h_p = 1.25h_w$. In moving bed catalyst regenerators, heat fluxes of the order of 25,000 Btu/(hr)(cuft) have been estimated to occur between fluid and particle. Fluid and particle temperatures consequently differ very little.

FLUIDIZED BEDS

A distinctive feature of fluidized beds is a high rate of heat transfer between the fluid and immersed surfaces. Some numerical values are shown on Figure 17.37. For comparison, air in turbulent flow in pipelines has a coefficient of about 25 Btu/(hr)(sqft)(°F). (a) is of calculations from several correlations of data for the conditions identified in Table 17.19; (b) shows the effect of diameters of quartz particles; and (c) pertains to 0.38 mm particles of several substances.

Temperature in a fluidized bed is uniform unless particle circulation is impeded. Gas to particle heat flow is so rapid that it is a minor consideration. Heat transfer at points of contact of particles is negligible and radiative transfer also is small below 600°C. The mechanisms of heat transfer and thermal conductivity have been widely studied; the results and literature are reviewed, for example, by Zabrodsky (1966) and by Grace (1982, pp. 8.65–8.83).

Heat transfer behavior is of importance at the walls of the vessel where it determines magnitudes of heat losses to the surroundings and at internal surfaces used for regulation of the operating temperature, although the old correlations for heat transfer coefficients of Wender and Cooper (1958) (shown on Figure 17.38) and those of Vreedenburg (1960) are still regarded as perhaps the best. (See Table 17.20.) A fair amount of scatter of the data obtained by various investigators is evident in Figure 17.38. Vreedenburg utilized additional data in his correlating, and, consequently, his figures show even more scatter. On Figure 17.37(a) also there is much disagreement; but note that if lines 8 and 9 by the same investigators and part of line 3 are ignored, the agreement becomes fair.

Some investigators are of the opinion that the correlations for vertical tubes should be taken as standard. Coefficients at the wall appear to be about 10% less than at vertical tubes on the axis

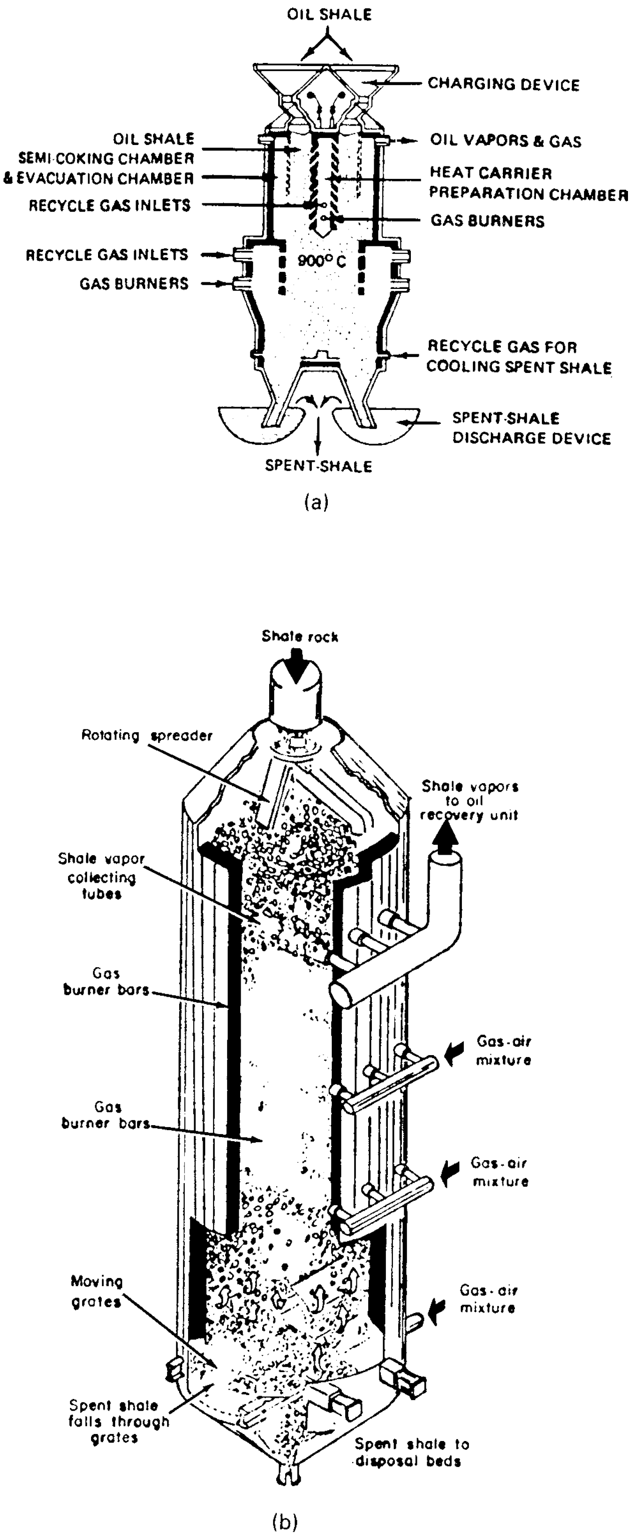


Figure 17.29. Moving bed reactors for cracking and recovery of shale oil. (a) Kiviter retort, USSR 200–300 tons/day (*Smith, in Meyers, 1984*). (b) Paraho retort for shale oil recovery (*Paraho Oil Shale Demonstration, Grand Junction, CO,* Walas, 1988).

of the vessel and those for horizontal tubes perhaps 5–6% less (Korotjanskaja et al., 1984, p. 315).

As appears on Figure 17.37(c), a peak rate of heat transfer is attained. It has been correlated by Zabrodsky et al. (1976) for particles smaller than 1 mm by the equation

$$h_{\max} d_s / k_g = 0.88\mathrm{Ar}^{0.213}, \ 100 < \mathrm{Ar} < 1.4 \times 10^5, \qquad (17.42)$$

$$\mathrm{Ar} = g\rho_g(\rho_s - \rho_g) d_s^3 / \mu_g^2. \qquad (17.43)$$

17.8. CLASSES OF REACTION PROCESSES AND THEIR EQUIPMENT

In this section, industrial reaction processes are classified primarily with respect to the kinds of phases participating, and examples are given of the kind of equipment that has been found suitable. As always, there is much variation in practice because of local or historical or personal circumstances which suggests that a certain latitude in new plant design is possible.

HOMOGENEOUS GAS REACTIONS

Ethylene was made by pyrolysis of hydrocarbon vapors in tubes of 50–100 mm dia and several hundred meters long with a reaction time of several seconds; heat was supplied by mixing with superheated steam and by direct contact of the tube with combustion gases.

Reactors to make polyethylene are 34–50 mm dia with 10–20 m long turns totalling 400–900 m in length. The tube is jacketed and heated or cooled at different positions with pressurized water.

A flow reactor is used for the production of synthesis gas, CO + H_2, by direct oxidation of methane and other hydrocarbons in the presence of steam. Preheated streams are mixed and react in a flow nozzle. Burning and quenching are performed in different zones of a ceramic-lined tower.

HOMOGENEOUS LIQUID REACTIONS

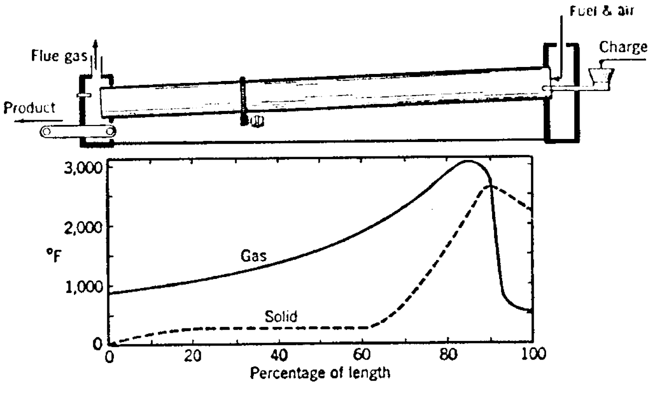
Almost innumerable instances of such reactions are practiced. Single-batch stirred tanks, CSTR batteries, and tubular flow reactors are all used. Many examples are given in Table 17.1. As already pointed out, the size of equipment for a given purpose depends on its type. A comparison has been made of the production of ethyl acetate from a mixture initially with 23% acid and 46% ethanol; these sizes were found for 35% conversion of the acid (Westerterp et al., 1984, pp. 41–58):

Reactor	V_r/V_0' [m^3/(kg/day)]
Batch (1/3 downtime)	1.04
PFR	0.70
CSTR	1.22
3-stage CSTR	0.85

Some of the homogeneous liquid systems of Table 17.1 are numbers 2, 16, 22, 28, 42, 53, 54, and 96, some in batch, mostly continuous.

LIQUID-LIQUID REACTIONS

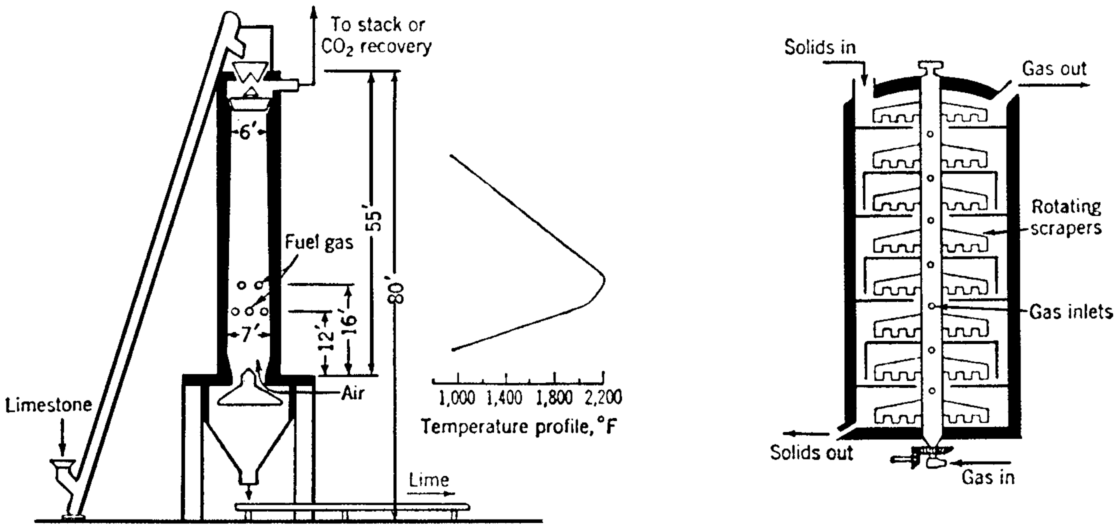
Such reactions can take place predominantly in either the continuous or disperse phase or in both phases or mainly at the interface. Mutual solubilities, distribution coefficients, and the amount of interfacial surface are factors that determine the overall rate of



(a)

Process	Lb/(hr)(cuft of kiln)
Cement, dry process	1.1–2.6
Cement, wet process, 44% water	0.7–1.7
Limestone calcination	1.1–2.1
Dolomite calcination	1.0–1.4
Alumina preparation	1.2–1.7
Barium sulfide preparation	0.9–2.0
Ignition of inorganic pigments	0.4–4.6
Iron pyrite roasting	0.7–0.9

(b)



(c) (d)

Figure 17.30. Kilns and hearth furnaces (Walas, 1988). (a) Temperature profiles in a rotary cement kiln. (b) Space velocities in rotary kilns. (c) Continuous lime kiln for production of approximately 55 tons/24 hr. (d) Multiple-hearth reactor; one with 9 trays, 16 ft dia and 35 ft high roasts 1250 lb/hr iron pyrite. (Walas, 1988).

conversion. Stirred tanks with power inputs of 5–10 HP/1000 gal or extraction-type equipment of various kinds are used to enhance mass transfer. Horizontal TFRs usually are impractical unless sufficiently stable emulsions can be formed, but mixing baffles at intervals are helpful if there are strong reasons for using such equipment. Multistage stirred chambers in a single shell have been used for example in butene-isobutane alkylation with sulfuric acid catalyst. Other liquid-liquid processes listed in Table 17.1 are numbers 8, 27, 45, 78, and 90.

GAS-LIQUID REACTIONS

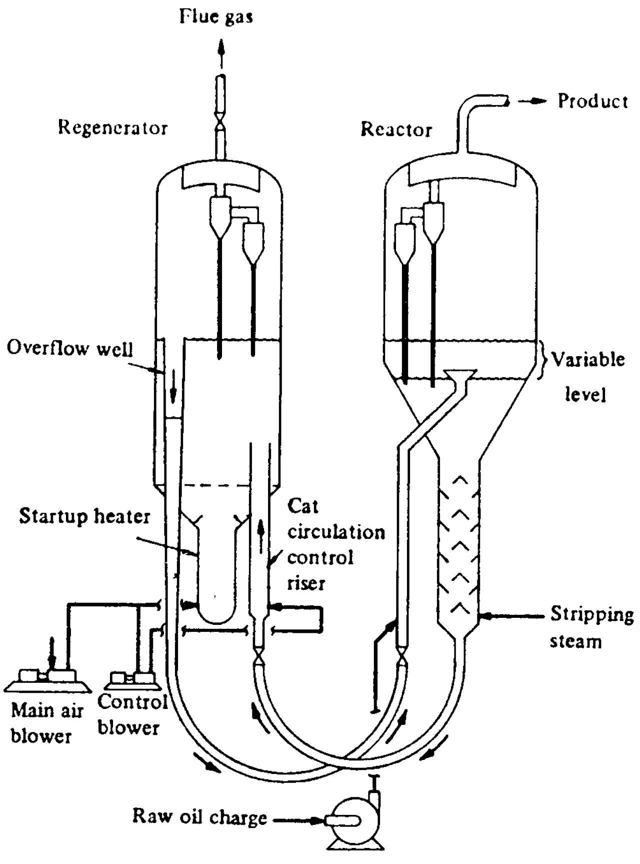
Intimate contacting between chemically reacting gas and liquid phases is achieved in a variety of equipment, some examples of which follow.

a. Tanks equipped with turbine agitators with or without internal gas recirculation. An example is air oxidation of cyclohexane to cyclohexanol and cyclohexanone.

b. Bubble towers with parallel flow of the phases, gas dispersed, with or without trays or packing. In such equipment isobutene from a mixture of C4 hydrocarbons forms tertiary butanol in contact with aqueous sulfuric acid.

c. Countercurrent flow of the two phases in tray or packed towers, as in ordinary absorption processes. Absorption of nitrogen oxides in water to make nitric acid is a prime example.

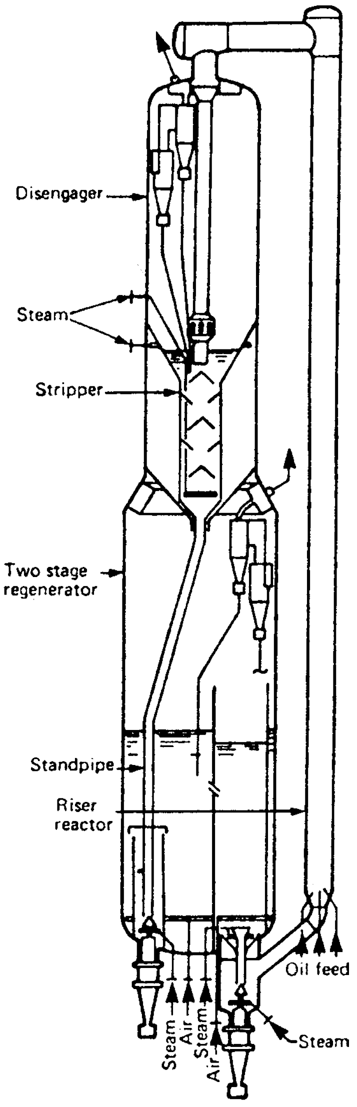
d. Tubular or multitubular reactors are usable when the volumetric rate of the gas is so much greater than that of the liquid that substantial mixing of phases exists. Adipic acid nitrile is made from gaseous ammonia and liquid adipic acid with a volumetric ratio of 1500; the residence time of the gas phase is about 1 sec, and that of the liquid 180–300 sec.



Typical FCC Operating Parameters

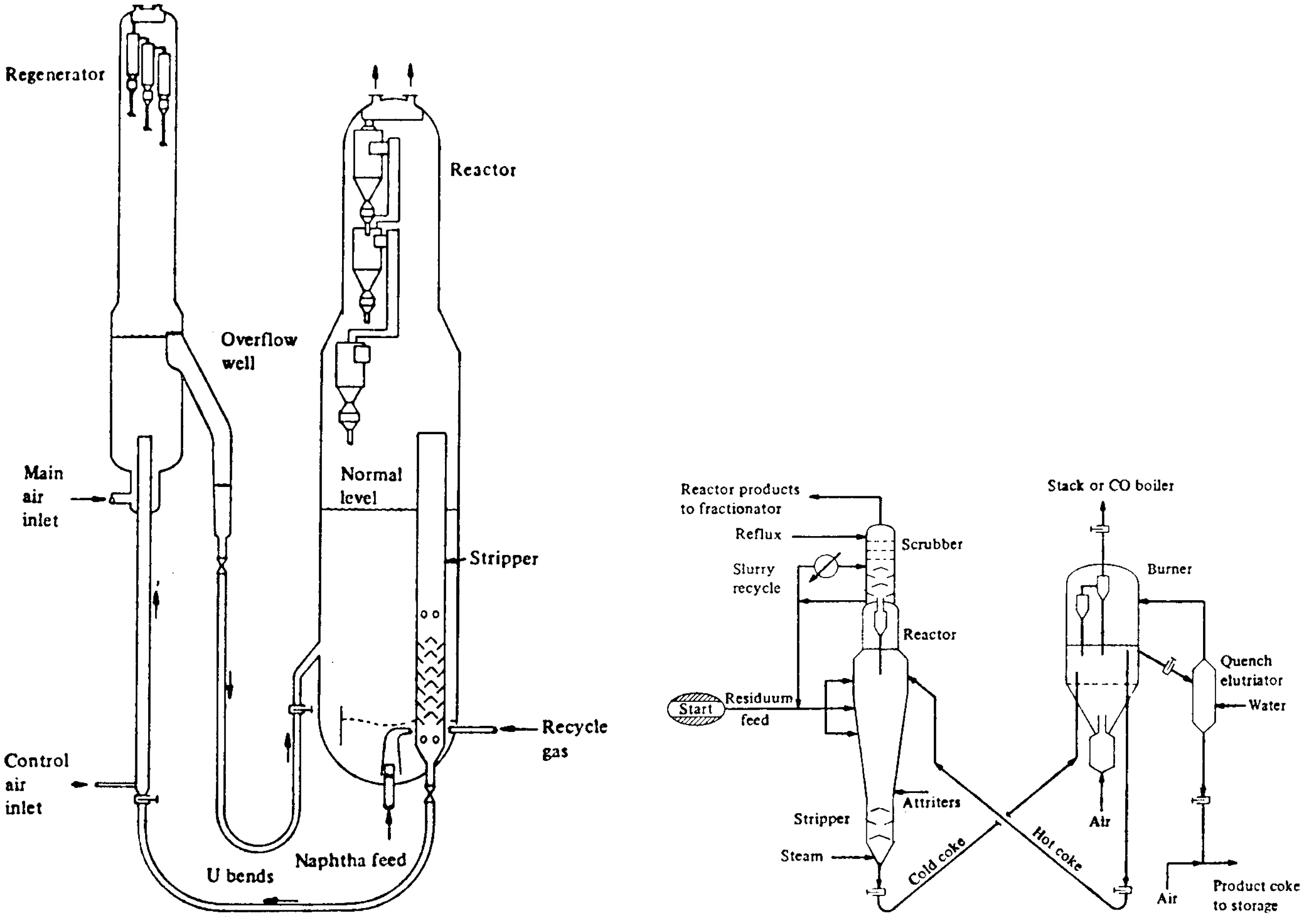
Parameter	Value
Feed capacity, kg/s	60 fresh; 95 total
Reactor diameter, m	6.7
Bed depth of reactor, m	Variable 0–1.6
Reactor dilute-phase velocity, m/s	0.75
Reactor temperature, °C	520
Stripper diameter, m	3.3
Stripper height, m	11
U-bend diameter, m	0.86
Catalyst circulation rate, kg/s	450
Regenerator diameter, m	10.7
Regenerator bed depth, m	6.64
Regenerator gas velocity, m/s	0.64
Height of regenerator cyclones inlet above bed, m	10.3
Regenerator temperature, °C	670
Regenerator pressure, kN/m^3 gauge	170
Catalyst inventory in regenerator, Mg	190
Entrainment to regenerator cyclones (estimated), kg/s	260
Catalyst losses in regenerator flue gas, g/s	15

(a)



(b)

Figure 17.31. Fluidized bed reactor processes for the conversion of petroleum fractions. (a) Exxon Model IV fluid catalytic cracking (FCC) unit sketch and operating parameters. (*Hetsroni, 1982*). (b) An FCC unit utilizing active zeolite catalysts; the reaction occurs primarily in the riser which can be as high as 45 m. (c) Fluidized bed hydroformer in which straight chain molecules are converted into branched ones in the presence of hydrogen at a pressure of 1500 atm. The process has been largely superseded by fixed bed units employing precious metal catalysts (*Hetsroni, 1982*). (d) A fluidized bed coking process; units have been built with capacities of 400–18,000 tons/day. (Walas, 1988).



(c)

(d)

Figure 17.31.—(*continued*)

- **e.** Liquid ejector for entraining the gas. This is used to remove dilute acid or other impurities from waste air by scrubbing with aqueous solutions; the liquid is recirculated so that a gas/liquid volumetric ratio of 100–200 is maintained.
- **f.** Pumps of centrifugal or turbine types are effective mixing devices and can constitute a reactor when the needed residence time is short. Such a device is used, for instance, to make acetic anhydride from acetic acid and ketene (Spes, 1966).
- **g.** Thin film reactors are desirable when the liquid viscosity is high, the reaction is highly exothermic and short reaction times are adequate. Such a process is the sulfonation of dodecylbenzene with dilute SO3 (Ujhidy et al., 1966).
- **h.** Packed tower reactors in parallel flow are operated either top-to-bottom or bottom-to-top. Distribution, holdup, and pressure drop behavior can be predicted from mass transfer correlations. Downflow towers have lower pressure drop, but upflow of liquid assures greater liquid holdup and longer contact time which often are advantages.

NONCATALYTIC REACTIONS WITH SOLIDS

The chief examples are smelting for the recovery of metals from ores, cement manufacture, and lime burning. The converters, roasters, and kilns for these purposes are huge special devices, not usually adaptable to other chemical applications. Shale oil is recovered from crushed rock in a vertical kiln on a batch or continuous basis—moving bed in the latter case—sometimes in a hydrogen-rich atmosphere for simultaneous denitrification and desulfurization. The capacity of ore roasters is of the order of 300–700 tons/(day)(m^3 of reactor volume). Rotary kilns for cement have capacities of 0.4–1.1 tons/(day)(m^3); for other purposes the range is 0.1–2.

FLUIDIZED BEDS OF NONCATALYTIC SOLIDS

Fluidized bed operations sometimes are alternates to those with fixed beds. Some of the successful processes are fluid bed combustion of coal, cracking of petroleum oils, ethylene production from gas oils in the presence of fluidized sand as a heat carrier, fluidized bed coking, water-gas production from coal (the original fluidized bed operation), recovery of shale oil from rock, reduction of iron ore with hydrogen at 30 atm pressure, lime burning, HCN from coke + ammonia + propane in a fluidized electric furnace, and many others. See Figures 17.31 and 17.32. Many of these processes have distinct equipment configurations and space velocities that cannot be generalized, except insofar as general relations apply to fluidized bed stability, particle size distribution, heat transfer, multistaging, and possibly other factors.

CIRCULATING GAS OR SOLIDS

High temperatures are generated by direct or indirect contact with combustion gases. A circulating bed of granular solids heated in this way has been used for the fixation of nitrogen from air in the range of 2300°C. Pebble heaters originally were developed as pyrolysis

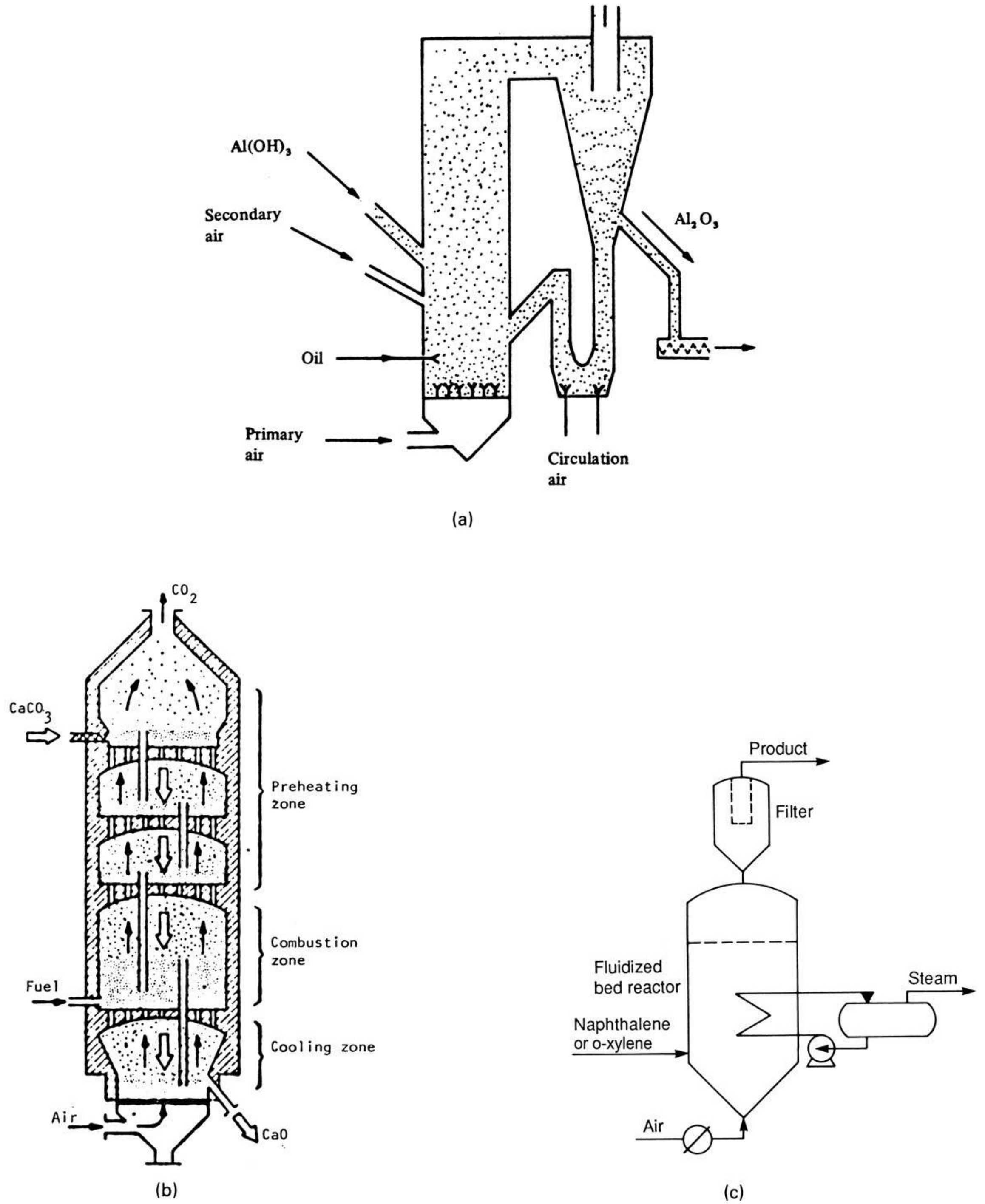
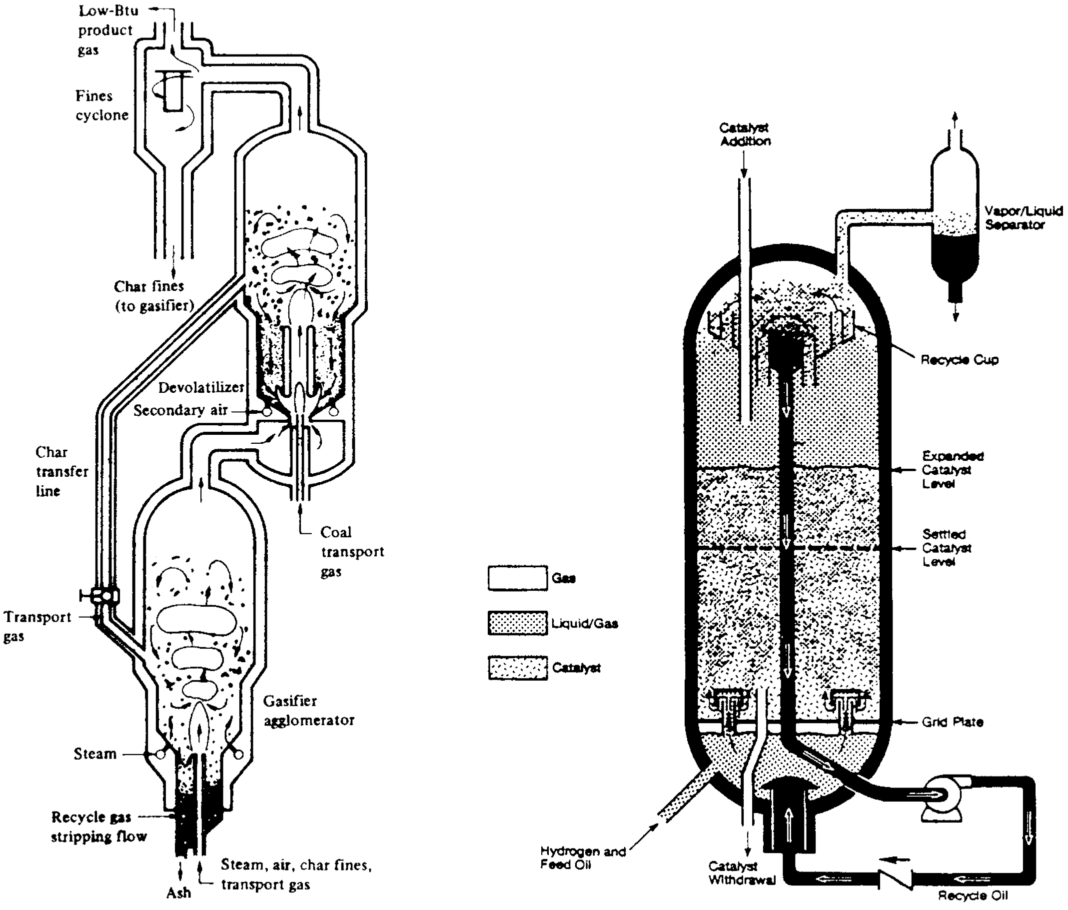


Figure 17.32. Other fluidized bed reaction systems. (a) Circulating fluidized bed process for production of alumina by calcination (*Lurgi*). (b) Multibed reactor for calcination of limestone (*Dorr-Oliver*). (c) Synthesis of phthalic anhydride; cooling surface is in the bed (*Badger-Sherwin-Williams*). (d) Coal gasifier with two beds to counteract agglomeration, with spent char recirculating at 20–30 times the fresh feed rate (*Westinghouse*). (e) Ebbulating bed reactor of the H-Coal and H-Oil process for converting these materials at high temperature and pressure into gas and lighter oils (*Meyer, 1984*). (Walas, 1988).



(d) (e)

Figure 17.32.—(*continued*)

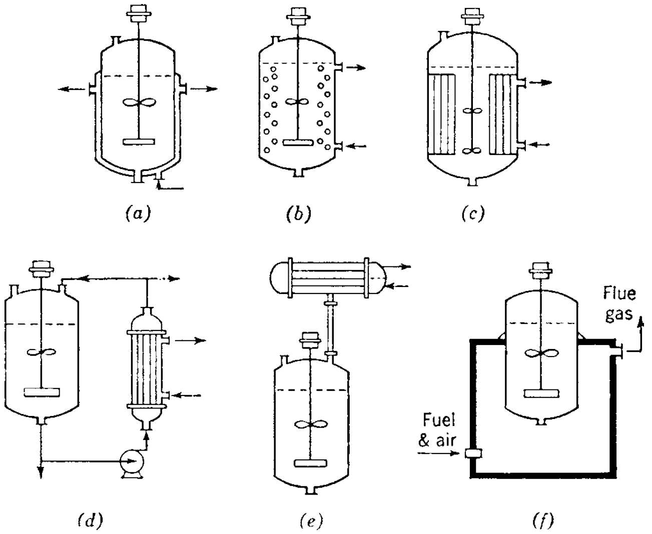


Figure 17.33. Heat transfer to stirred-tank reactors: (a) jacket; (b) internal coils; (c) internal tubes; (d) external heat exchanger; (e) external reflux condenser; (f) fired heater. Note: See also Fig. 17.9(e) and (f). (Walas, 1988).

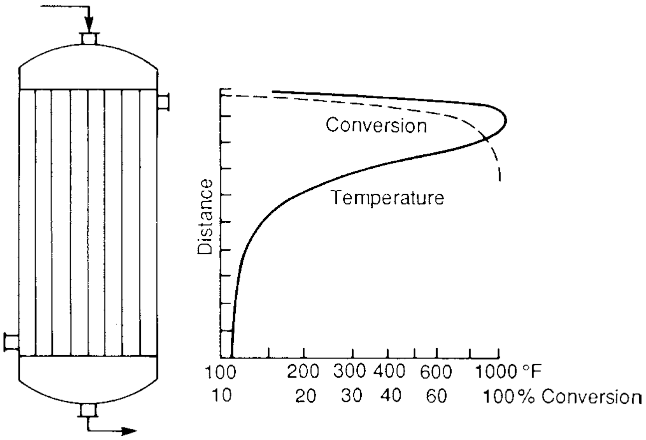


Figure 17.34. Temperature and conversion profiles in a water-cooled shell-and-tube phosgene reactor, 2-in. tubes loaded with carbon catalyst, equimolal CO and Cl_2. (Walas, 1988).

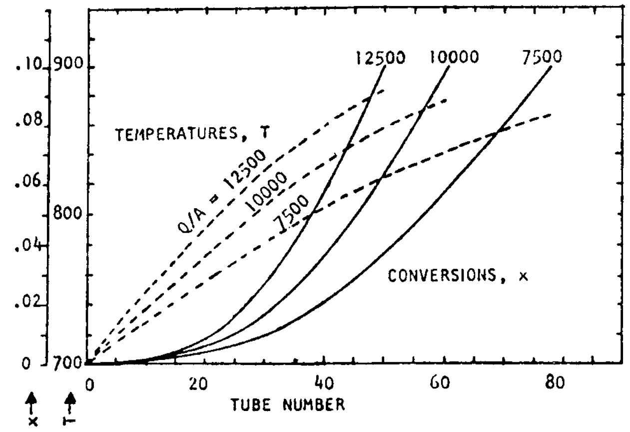


Figure 17.35. Temperature and conversion profiles of mild thermal cracking of a heavy oil in a tubular furnace with a back pressure of 250 psig and at several heat fluxes [Btu/hr(sqft)].

reactors to make ethylene, but are no longer used for this purpose. Pebbles are 5–10 mm dia, temperatures of 1700°C are readily attained, heat fluxes are in the vicinity of 15,000 Btu/(hr)(°F)(cuft of pebbles) and contact times are fractions of a second. These characteristics should be borne in mind for new processes, although there are no current examples. Induction heating of fluidized particles has been used to transfer heat to a reacting fluid; in this process the solid remains in the reactor and need not circulate through a heating zone.

FIXED BED SOLID CATALYSIS

This kind of process is used when the catalyst maintains its activity sufficiently long, for several months or a year or two as in the cases of some catalytic reforming or ammonia synthesis processes. A few processes have operated on cycles of reaction and regeneration of less than an hour or a few hours. Cycle timers on automatic valves make such operations completely automatic. A minimum of three vessels usually is needed: One on-stream, one being regenerated, and the last being purged and prepared for the next cycle. Adsorption processes are conducted this way. The original Houdry cracking process employed 10 min on-stream. One catalytic reforming process employs seven or so reactors with one of them down every week. Regeneration usually is done in place, but eventually the catalyst must be removed and replaced. Platinum and other precious metals are recovered from the catalyst carriers in the factory.

A granular catalyst sometimes serves simultaneously as tower packing for reaction and separation of the participants by distillation, particularly when the process is reversible and removal of the product is necessary for complete conversion to take place. This is the case of the reaction of methanol and isobutene to make methyl tertiary-butyl ether (MTBE) in the presence of granular acid ion exchange resin catalyst. MTBE is drawn off the bottom of the tower and excess methanol off the top. Such a process is applicable when the reaction can be conducted satisfactorily at boiling temperatures; these can be adjusted by pressure.

A variety of provisions for temperature control of fixed beds is described in Section 17.6 and following.

a. Single beds are used when the thermal effects are small. Jacketed walls usually are inadequate for heat transfer to beds, but embedded heat transfer tubes sometimes are used.
b. Multitubular units with catalyst in tubes and heat transfer medium on the shell side are popular. A reactor for making phosgene from carbon monoxide and chloride has 2-in. dia tubes 8 ft long filled with activated carbon catalyst and cooling water on the shell side.
c. Multibed units with built-in interstage heat transfer surface. These units are economical when the amount of surface is not large. In comparison with type (d) of Figure 17.13, this design may have more difficult maintenance, less flexibility and higher cost because of the shortness of the tubes that may have to be used. The Sper-Rashka converter for SO2 oxidation has three beds and three large internal exchangers in a single shell (Ullman, 3rd ed., 1964, Vol. 15, p. 456).
d. Multibed units with external heat exchangers. Several variations of this design with steam generation or feed gas as means of cooling are used for the catalytic oxidation of SO2.
e. Multibed unit with interstage injection of temperature controlled process fluid or inert fluid for temperature control of the process. In the synthesis of cumene from propylene and benzene in the presence of supported phosphoric acid catalyst, interstage injection of cold process gas and water is used for temperature control and maintenance of catalyst activity (Figure 17.18(g)).
f. Autothermal multitubular unit with heat interchange between feed on the shell side and reacting gas in the packed tubes and between feed and reacted gas in an external or built-in exchanger. Many complex variations of this design have been or are being used for ammonia synthesis.
g. Multibed units in individual shells with interstage heat transfer. From three to seven stages are adopted by different processes for the catalytic reforming of naphthas to gasoline.

FLUIDIZED BED CATALYSIS

Such processes may be conducted to take advantage of the substantial degree of uniformity of temperature and composition and high rates of heat transfer to embedded surfaces. O-toluene is a raw material for the production of phthalic anhydride. Orthophthalic anhydride is made by oxidation of naphthalene in a fluidized bed of V_2O_5 deposited on silica gel with a size range of 0.1–0.3 mm with a contact time of 10–20 sec at 350–380°C. Heat of reaction is removed by generation of steam in embedded coils. No continuous regeneration of catalyst is needed. Acrylonitrile and ethylene dichloride also are made under conditions without the need for catalyst regeneration.

From the standpoint of daily capacity, the greatest application of fluidized bed catalysis is to the cracking of petroleum fractions into the gasoline range. In this process the catalyst deactivates in a few minutes, so that advantage is taken of the mobility of fluidized catalyst to transport it continuously between reaction and regeneration zones in order to maintain its activity; some catalyst also must be bled off continuously to maintain permanent poisons such as heavy metal deposits at an acceptable level.

Several configurations of reactor and regenerator have been in use, two of which are illustrated in Figures 17.31(a) and (b). Part (a) shows the original arrangement with separate vessels side by side for the two operations. The steam stripper is for removal of occluded oil from the catalyst before it is burned. In other designs the two vessels are in vertical line, often in a single shell with a partition. Part (b) is the design of transfer line cracking which employs highly active zeolite catalysts that are effective at short contact times. The upper vessel is primarily a catalyst disengaging zone. A substantial gradient develops in the transfer line and results in an improvement in product distribution compared with that from mixed reactors such as part (a).

Tube		Formula (D_p and D_t in m)	Range of $N_{Re'}$ or other variable	Remarks
Diameter, D_t, mm	**Length L, m**			
100 square	1	$N_{pe'} = 2.4 \text{ to } 6.3$	$G \simeq 1000 \text{kg/m}^2\text{h}$	
100	0.2–0.4	Graphs in paper	Gas velocity: 2500–7200 m/h	Special apparatus at low velocities
50	0.05–0.2	$\frac{k_r}{k_g} = 5.0 + 0.061\left(\frac{D_p G}{\mu}\right)$	30–100	
50–100		$\frac{k_r}{k_g} = 10.0 + 0.0267\left(\frac{G}{\mu a_v}\right); h_w = 2.07\left(\frac{G}{\mu a_v}\right)^{0.47}$	20–500	
127	up to 1	$k_r = 0.27 + 0.00146\frac{\sqrt{a_p G}}{\mu}; h_w = 8.51\, G^{0.33}$	$G(\text{kg} = \text{m}^2\text{h})$: 850–6000	
25–100	0.1–0.4	$\frac{k_r}{k_g} = \begin{cases} 5.5 + 0.05\left(\frac{D_p G}{\mu}\right) \\ 1.72\left(\frac{D_p G}{\mu}\right)^{0.41} \\ 0.209\left(\frac{D_p G}{\mu}\right)^{0.87} \end{cases}$	0–30 30–100 100–1000	See also Hatta and Maeda (1948 a, b, 1949), Maeda (1950), and Maeda and Kawazoe (1953)
41	0.75	$K_r = 0.36 + 0.00162\left(\frac{D_p G}{\mu}\right); h_w = 0.04\, G$	30–1100 $500 < G < 17000$	
65	0.3	$\frac{k_r}{k_g} = 10.5 + 0.076 N_{\text{pr}}\left(\frac{4G}{\mu a_v}\right); \frac{h_w D_p}{K_g} = 0.155 N_{\text{pr}^{\frac{1}{3}}}\left(\frac{4G}{\mu a_v}\right)^{0.75}$	10–3500 150–4000	For rings see paper
35–95	0.16–0.32	$\frac{k_r}{k_g} = 1.23\left(\frac{\sqrt{a}_p G}{\mu}\right)^{0.43}$ No correction for h_w	100–3000	The first paper gives a slightly different formula for cooling
50	0.3	See graph in paper. No correction for h_w	400–3500	
30–50	0.2–0.3	$\frac{k_r}{k_g} = \frac{k_{r,0}}{k_g} + 0.10(a_V Dt)^{0.50}\left(\frac{G}{\mu a_v}\right)^{0.69}$	10–1000	No correction for hw
50		Graph in paper of N'_{Pe} vs. N'_{Re}	5–2400	Diffusion of methylene blue in water

[a] a_p = surface of a particle, a_v = surface/volume in the bed. (Kjaer, 1958).

Hundreds of fluidized bed crackers are in operation. The vessels are large, as much as 10 m or so in diameter and perhaps twice as high. Such high linear velocities of vapors are maintained that the entire catalyst content of the vessels circulates through the cyclone collectors in an hour or so. Electrical precipitators after the cyclone collectors have been found unnecessary.

Two other fluidized bed petroleum reactors are illustrated as Figures 17.31(c) and (d) and several nonpetroleum applications in Figure 17.32.

GAS-LIQUID REACTIONS WITH SOLID CATALYSTS

The number of commercial processes of this type is substantial. A brief list arranged according to the kind of reactor is in Table 17.21. Depending on the circumstances, however, it should be noted that some reactions are conducted industrially in more than one kind of reactor.

Leading characteristics of five main kinds of reactors are described following. Stirred tanks, fixed beds, slurries, and three-phase fluidized beds are used. Catalyst particle sizes are a compromise between pressure drop, ease of separation from the fluids, and ease of fluidization. For particles above about 0.04 mm dia, diffusion of liquid into the pores and, consequently, accessibility of the internal surface of the catalyst have a minor effect on the overall conversion rate, so that catalysts with small specific surfaces, of the order of 1 m^2/g, are adequate with liquid systems. Except in trickle beds the gas phase is the discontinuous one. In some operations of bubble towers, the catalyst remains in the vessel, although minor amounts of catalyst entrainment may occur.

1. Stirred tanks with suspended catalyst are used both in batch and continuously. Hydrogenation of fats or oils with Raney nickel or of caprolactam usually are in batch. Continuous processes include some hydrogenations of fats, some fermentation processes with cellular enzymes and air and the hydrogenation of nitrogen monoxide to hydroxylamine. The gas is distributed with spargers or introduced at the eye of a high-speed impeller in a draft tube. Internal recirculation of the gas also is practiced. The power input depends on the settling tendency of the particles and the required intimacy of gas-liquid mixing. It is greater than in the absence of solids; for example, the solid catalyzed hydrogenation of nitrogen monoxide employs a power input of about 10 kW/m3 (51 HP/1000 gal) compared with 5–10 HP/1000 gal for ordinary liquid-liquid mixing.
2. In ebullated (liquid fluidized) beds the particles are much larger (0.2–1 mm) than in gas fluidization (0–0.1 mm). Little expansion of the bed occurs beyond that at minimum fluidization, so that the bed density is essentially the same as that of the fixed bed. Because substantial internal circulation of the liquid is needed to maintain fluidization, the fluids throughout the reactor are substantially uniform. In the hydrodesulfurization and hydrocracking of petroleum fractions and residua at 100 atm

TABLE 17.10. Overall Heat Transfer Coefficients in Agitated Tanks [*U* Btu/(hr)(sqft)(°F)]

Fluid Inside Jacket	Fluid In Vessel	Wall Material	Agitation	*U*
Steam	water	enameled cast iron	0–400 rpm	96–120
Steam	milk	enameled C.I.	none	200
Steam	milk	enameled C.I.	stirring	300
Steam	milk boiling	enameled C.I.	none	500
Steam	milk	enameled C.I.	200 rpm	86
Steam	fruit slurry	enameled C.I.	none	33–90
Steam	fruit slurry	enameled C.I.	stirring	154
Steam	water	C.I. and loose lead lining	agitated	4–9
Steam	water	C.I. and loose lead lining	none	3
Steam	boiling SO_2	steel	none	60
Steam	boiling water	steel	none	187
Hot water	warm water	enameled C.I.	none	70
Cold water	cold water	enameled C.I.	none	43
Ice water	cold water	stoneware	agitated	7
Ice water	cold water	stoneware	none	5
Brine, low velocity	nitration slurry	—	35–58 rpm	32–60
Water	sodium alcoholate solution	"Frederking" (cast-incoil)	agitated, baffled	80
Steam	evaporating water	copper	—	381
Steam	evaporating water	enamelware	—	36.7
Steam	water	copper	none	148
Steam	water	copper	simple stirring	244
Steam	boiling water	copper	none	250
Steam	paraffin wax	copper	none	27.4
Steam	paraffin wax	cast iron	scraper	107
Water	paraffin wax	copper	none	24.4
Water	paraffin wax	cast iron	scraper	72.3
Steam	solution	cast iron	double scrapers	175–210
Steam	slurry	cast iron	double scrapers	160–175
Steam	paste	cast iron	double scrapers	125–150
Steam	lumpy mass	cast iron	double scrapers	75–96
Steam	powder (5% moisture)	cast iron	double scrapers	41–51

(LIGHTNIN Technology Seminar, Mixing Equipment Co., 1982).

TABLE 17.11. Jacketed Vessels Overall Heat Transfer Coefficients

			Overall U*	
Jacket Fluid	Fluid in Vessel	Wall Material	Btu/(h · ft^2 · °F)	J/(m^2 · s · k)
Steam	Water	Stainless steel	150–300	850–1700
Steam	Aqueous solution	Stainless steel	80–200	450–1140
Steam	Organics	Stainless steel	50–150	285–850
Steam	Light oil	Stainless steel	60–160	340–910
Steam	Heavy oil	Stainless steel	10–50	57–285
Brine	Water	Stainless steel	40–180	230–1625
Brine	Aqueous solution	Stainless steel	35–150	200–850
Brine	Organics	Stainless steel	30–120	170–680
Brine	Light oil	Stainless steel	35–130	200–740
Brine	Heavy oil	Stainless steel	10–30	57–170
Heat-transfer oil	Water	Stainless steel	50–200	285–1140
Heat-transfer oil	Aqueous solution	Stainless steel	40–170	230–965
Heat-transfer oil	Organics	Stainless steel	30–120	170–680
Heat-transfer oil	Light oil	Stainless steel	35–130	200–740
Heat-transfer oil	Heavy oil	Stainless steel	10–40	57–230
Steam	Water	Glass-lined CS	70–100	400–570
Steam	Aqueous solution	Glass-lined CS	50–85	285–480
Steam	Organics	Glass-lined CS	30–70	170–400
Steam	Light oil	Glass-lined CS	40–75	230–425
Steam	Heavy oil	Glass-lined CS	10–40	57–230
Brine	Water	Glass-lined CS	30–80	170–450
Brine	Aqueous solution	Glass-lined CS	25–70	140–400
Brine	Organics	Glass-lined CS	20–60	115–340
Brine	Light oil	Glass-lined CS	25–65	140–370
Brine	Heavy oil	Glass-lined CS	10–30	57–170
Heat-transfer oil	Water	Glass-lined CS	30–80	170–450
Heat-transfer oil	Aqueous solution	Glass-lined CS	25–70	140–400
Heat-transfer oil	Organics	Glass-lined CS	25–65	140–370
Heat-transfer oil	Light oil	Glass-lined CS	20–70	115–400
Heat-transfer oil	Heavy oil	Glass-lined CS	10–35	57–200

*Values listed are for moderate nonproximity agitation. CS = carbon steel.
(*Perry's Chemical Engineers' Handbook*, 6th ed., McGraw-Hill, New York, 1984, Table 10–14, p. 10–46). (Walas, 1988).

TABLE 17.12. Overall Heat Transfer Coefficients with Immersed Coils [*U* expressed in Btu/(h · ft^2 · °F)

Type of coil	Coil spacing, in. †	Fluid in coil	Fluid in vessel	Temp. range, °F.	*U*‡ without cement	*U* with heat-transfer cement
3/8 in. o.d. copper tubing attached with bands at 24-in. spacing	2	5 to 50 lb./sq. in. gage steam	Water under light agitation	158–210	1–5	42–46
	3 1/8			158–210	1–5	50–53
	6 1/4			158–210	1–5	60–64
	12 1/2 or greater			158–210	1–5	69–72
3/8 in. o.d. copper tubing attached with bands at 24-in. spacing	2	50 lb./sq. in. gage steam	No. 6 fuel oil under light agitation	158–258	1–5	20–30
	3 1/8			158–258	1–5	25–38
	6 1/4			158–240	1–5	30–40
	12 1/2 or greater			158–238	1–5	35–46
Panel coils		50 lb./sq. in. gage steam	Boiling water	212	29	48–54
		Water	Water	158–212	8–30	19–48
		Water	No. 6 fuel oil	228–278	6–15	24–56
			Water	130–150	7	15
			No. 6 fuel oil	130–150	4	9–19

Data courtesy of Thermon Manufacturing Co. (Walas, 1988).

†External surface of tubing or side of panel coil facing tank.

TABLE 17.13. Summary of Heat-Transfer Coefficients on the Agitated Side

General Equation: $\frac{h(L)}{\lambda_f} = \alpha\left(\frac{\rho N D_1^2}{\mu}\right)^m \left(\frac{c_\rho \mu}{\lambda_f}\right)^b \left(\frac{\mu_b}{\mu_w}\right)^c$ **(other terms)**

Agitator Type	Transfer Surface	Approx. Reynolds Number Range	*L*	*α*	*m*	*b*	*c*	Other Terms	Additional Comments	Ref.
Turbine 6-blade, flat (baffled)	jacket	$10–10^5$	*D*	0.73	0.65	0.33	0.24	—	Use for standard configuration.	1,25
	coil	$400 - 1.5 \times 10^6$	d_{ct}	0.17	0.67	0.37	See Note 1	$\left(\frac{D_1}{D}\right)^{0.1}\left(\frac{d_{et}}{D}\right)^{0.5}$	See p. 357 for details See Note 2. Applies for standard configuration with $D_c/D = 0.7$ and $S_c/d_{ct} = 2 - 4$; $Z_c/D = 0.15$	29
	vertical baffle-type	$10^3 - 2 \times 10^6$	d_{ct}	0.09	0.65	0.33	0.4	$\left(\frac{D_1}{D}\right)^{0.33}\left(\frac{2}{n_{vb}}\right)^{0.2}$		32
6-blade, retreating blade (curved blade)	jacket	$10^3 - 10^6$	*D*	0.68	0.67	0.33	0.14		Revised. See Note 3	27,30
no baffles	coil	$10^3 - 10^6$	d_{ct}	1.40	0.62	0.33	0.14	—	Revised	27,30
6-blade, 45° pitched	jacket	20–200	*D*	0.44[a]	0.67	0.33	0.24	—	Baffles have no effect in Reynolds number range studied in 12-in diameter vessel	33
3-blade retreating	jacket	$2 \times 10^4 - 2 \times 10^6$	*D*	0.37[b]	0.67	0.33	0.14	—	For glass-lined vessels with finger-type baffle	27
Propeller	jacket	2×10^3	*D*	0.54	0.67	0.25	0.14	—	Limited data, but a large 5 ft diameter tank used, marine-type impeller used at 458 pitch and located at the midpoint of tank.	34
Paddle	jacket	$600 - 5 \times 10^5$	*D*	0.112	0.75	0.44	0.25	$\left(\frac{D}{D_1}\right)^{0.40}\left(\frac{w_1}{D_1}\right)^{0.13}$	No baffles used	26,35
	coil	$3 \times 10^2 - 2.6 \times 10^5$	d_{ct}	0.87	0.62	0.33	0.14	—		37
Anchor	jacket	10–300	*D*	1.0	0.5	0.33	0.18	—		34,36
		300–40,000	*D*	0.36	0.67	0.33	0.18	—		34,36

Notes.

1. $\ln c = -0.202 \ln \mu - 0.357$, with μ in cp.
2. For unbaffled case with coils use 0.65 of h calculated for baffled case (29).
3. With baffles and $N_{Re} < 400$ use value calculated. In fully developed turbulent region baffles increase calculated h by approximately 37% (1)

New nomenclature: d_{ct} is outside tube diameter of coil, D_c is coil diameter, n_{bv} is number of vertical baffle-type coils, S_c is coil spacing, w_1 is impeller blade width, and Z_c is height of coil from tank bottom.

[a] For impeller $4\frac{1}{2}$-in. from bottom, 0.535 for impeller 11-in from bottom

[b] For steel impeller, 0.33 for glassed-steel impeller

(Rase, 1977, Vol. 1). (Walas, 1988).

TABLE 17.14. Equations for Heat Transfer Coefficients inside Stirred Tanks[a]

1. To jackets, with paddles, axial flow, and flat blade turbines[1,6,7]

$$h_0(\text{jacket})\frac{T}{k} = 0.85\left(\frac{D^2N\rho}{\mu}\right)^{0.66}\left(\frac{C_p\mu}{k}\right)^{0.33} \times\left(\frac{\mu}{\mu_s}\right)^{0.14}\left(\frac{Z}{T}\right)^{-0.56}\left(\frac{D}{T}\right)^{0.13}$$

2. To helical coils[3,5]

$$h_0(\text{coil})\frac{D}{k} = 0.17\left(\frac{D^2N\rho}{\mu}\right)^{0.67}\left(\frac{C_p\mu}{k}\right)^{0.37}\times\left(\frac{D}{T}\right)^{0.1}\left(\frac{d}{T}\right)^{0.5}\left(\frac{\mu}{\mu_s}\right)^{m}$$

$$m = 0.714/\mu^{0.21}, \mu \text{ in } cP$$

3. To vertical tubes[2]

$$h_0(\text{tubes})\frac{D}{K} = 0.09\left(\frac{D^2N\rho}{\mu}\right)^{0.65}\left(\frac{C_p\mu}{k}\right)^{0.3} \times\left(\frac{D}{T}\right)^{0.33}\left(\frac{2}{n_b}\right)^{0.2}\left(\frac{\mu}{\mu_s}\right)^{0.14}$$

4. To plate coils[4]

$$h_0\,(\text{plate coil})\frac{L}{K} = 0.1788\left(\frac{ND^2\rho}{\mu}\right)^{0.448}\left(\frac{C_p\mu}{k}\right)^{0.33}\left(\frac{\mu}{\mu_f}\right)^{0.50}$$

$$\text{for } N_{\text{Re}} < 1.4\times10^3$$

$$h_0\,(\text{plate coil})\frac{L}{K} = 0.0317\left(\frac{ND^2\text{p}}{\mu}\right)^{0.658}\left(\frac{C_p\mu}{k}\right)^{0.33}\left(\frac{\mu}{\mu_f}\right)^{0.50}$$

$$\text{for } N_{\text{Re}} > 4\times10^3$$

[a] Nomenclature: d = tube diameter, D = impeller diameter, L = plate coil height, N = impeller rotational speed, n_b = number of baffles or of vertical tubes acting as baffles, T = tank diameter, Z = liquid height.

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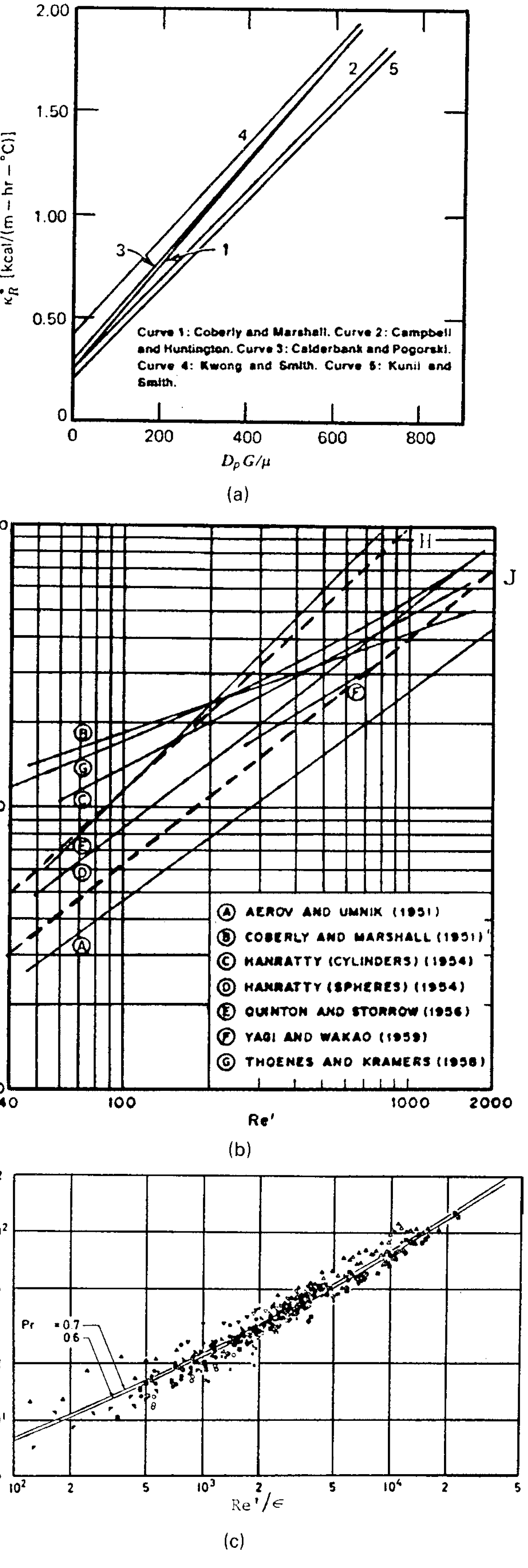


(a)

(b)

(c)

Figure 17.36. Effective thermal conductivity and wall heat transfer coefficient of packed beds. $\text{Re}' = d_pG/\mu, d_p = 6V_p/A_p, \varepsilon =$ porosity. (a) Effective thermal conductivity in terms of particle Reynolds number. Most of the investigations were with air of approx. $k_f' = 0.026$, so that in general $k_e'/k_f' = 38.5k'$ (*Froment*, 1970). (b) Heat transfer coefficient at the wall. Recommendations for L/d_p above 50 by Doraiswamy and Sharma are line H for cylinders, line J for spheres. (c) Correlation of Gnielinski (*cited by Schlünder, 1978*) of coefficient of heat transfer between particle and fluid. The wall coefficient may be taken as $h_w = 0.8h_p$. (Walas, 1988).

TABLE 17.15. Data for the Effective Thermal Conductivity, K_r (kcal/mh°C), and the Tube Wall Film Coefficient, h_w (kcal/ m^2h°C), in Packed Beds[a]

Authors	Method of Measurement	Heating or Cooling of Gas	Gas	Particles		
				Material	Shape	Diameter D_p, mm
Bakhurov and Boreskov (1947)	Radial temperature and concentration profiles	C	Air	Glass, porcelain, metals, etc.	Spheres, rings, cylinders, granules	3–19
Brötz (1951)	″	H	N_2, CO_2, H_2	Glass, catalyst	Spheres, granules	2–10
Bunnell, Irvin, Olson, and Smith (1949)	Radial temperature profiles	C	Air	Alumina	Cylinders	3
Campbell and Huntington (1952)	″	H, C	Air, natural gas (82% CH_4	Glass, alumina, aluminum	Spheres, cylinders	5–25
Coberly and Marshall (1951)	″	H	Air	Celite	Cylinders	3–12
Maeda (1952)	″	C	Air	Catalyst	Cylinders	3–10
Quinton and Storrow (1956)	″	H	Air	Glass	Spheres	4.4
Aerov and Umnik (1951b, c)	Packed bed heat exchanger. Single radial temperature	C	Air, CO_2, H_2	Glass, catalyst, porcelain, sand	Spheres, tablets, rings	0.4–10
Hougen and Piret (1951), Molino and Hougen (1952)	Packed bed heat exchanger	C H	Air	Celite	Spheres, cylinders	2–12
Kling (1938b)	″	H	Air	Steel, glass	Spheres	3–4
Verschoor and Schuit (1950)	″	H	Air, H_2	Lead, glass, etc.	Spheres, cylinders, granules	3–10
Bernard and Wilhelm (1950)	Mass diffusion		(Water)	Glass, lead, alumina, etc.	Spheres, cylinders, granules	1–8

and 400°C, a temperature variation of only 2°C or so is obtained in the reactor.

3. Slurry reactors (bubble towers) are fluidized with continuous flow of gas. The particles are smaller (less than 0.1 mm) than in the liquid fluidized systems (0.2–1 mm). In some operations the liquid and solid phases are stationary, but in others they circulate through the vessel. Such equipment has been used in Fischer-Tropsch plants and for hydrogenation of fatty esters to alcohols, furfural to furfuryl alcohol, and of glucose to sorbitol. Hydrogenation of benzene to cyclohexane is done at 50 bar and 220–225°C with Raney nickel of 0.01–0.1 mm dia. The relations between gas velocities, solids concentrations, bubble sizes, and rates of heat transfer are extensively documented in the literature.
4. In trickle bed reactors the gas and liquid both flow downward through a fixed bed of catalyst. The gas phase is continuous, and the liquid also is continuous as a film on the particles. Provided that the initial distribution is good, liquid distribution remains substantially uniform at rates of 10–30 m3/m2 hr superficially, but channelling and hot spots may develop at lower rates. Redistributors sometimes are used. The many correlations that have been developed for packed bed mass transfer are applicable to trickle bed operation. Commercial reactors are 1–4 m dia and 10–30 m long. Hydrocracking and hydrodesulfurization of petroleum and hydration of olefins are commonly practiced in trickle beds at superficial liquid velocities of 3–90 m/hr.
5. Upflow fixed beds. The liquid phase is continuous and the gas phase dispersed. This mode of operation has the advantages of better mixing, higher rates of mass and heat transfer, better distribution of liquid flow across the cross section, and better scouring of deactivating deposits from the surface of the catalyst. The disadvantages relative to trickle beds are higher pressure drop, the possibility of occurrence of flooding, and the need for mechanical restraint to prevent fluidization and entrainment of the catalyst. The most prominent example of upflow operation is the SYNTHOIL coal liquefaction process, but this mode of operation is competitive in other cases with the trickle bed, depending on the balance of advantages and disadvantages in particular situations.

Because of the increased interest in developing biochemical reactions to produce alternative fuels, pharmaceuticals and bio-chemicals, there have been a large number of unique designs for the production of these chemical products. However, most of the designs are of small scale and, as yet, are not suitable for economic large-scale manufacturing. At present, most pharmaceuticals and specialty chemicals are manufactured in large-scale adaptations of CSTR like the fermenter in Figure 17.40 or in plug flow equipment mentioned earlier in this chapter.

TABLE 17.15.—(*continued*)

Tube				
Diameter, D_t, mm	**Length L, m**	**Formula (D_p and D_t in m)**	**Range of $N_{Re'}$ or other variable**	**Remarks**
150–230	0.5–1	$h_v = A\frac{G^{0.7}}{D_p{}^{0.9}}T^{0.3}10^{1.68\varepsilon - 3.56\varepsilon^2}$	Range of G (kg/m^{2}h): 2300–9200	A given in paper. Corrections for temperature and voids not very reliable
ca. 300 square	0.9	$h_v = 1.82\left(\frac{G}{D_p}\right)^{0.7}$	G: 300–1600	
50–200	0.09–0.34	Graphs in paper	G: 2670–5340	Correlated by Löf and Hawley (1948) as: $h_v = 0.152\,\frac{G}{D_p}$
	0.01–0.25	Graphs and $\frac{hDp}{k_g} = 0.24\left(\frac{D_pG}{\mu}\right)^{0.83}$	Gas velocity: 0.7–2 m/sec.	
	0.05	Graphs in paper	100–1000	
350		$\frac{hD_p}{K_g} = A\left(\frac{D_pG}{\mu}\right)^{0.61}$	130–2000	A varies from 0.590 to 0.713. See also Glaser (1938)
		$j_h = \frac{h}{GC_p}N_{\text{pr}^{\frac{2}{3}}} = 1.064\left(\frac{D_pG}{\mu}\right)^{-0.41}$	350–4000	
		$j_h = \frac{h}{GC_p}N_{\text{pr}^{\frac{2}{3}}} = 1.96\left(\frac{D_pG}{\mu}\right)^{-0.51}$ Rings: $j_h = 1.148\left(\frac{\sqrt{a}_pG}{\mu}\right)^{-0.41}$ Saddles: $j_h = 0.920\left(\frac{\sqrt{a}_pG}{\mu}\right)^{-0.34}$	50–350 100–20000 70–3000	
38 square		Graphs in paper	1–18	
47–75	0.024	$j_h = 0.992\left(\frac{D_pG}{\mu}\right)^{-0.34}$	15–160	

[a] a_p = surface of a particle, a_v = surface/volume in the bed. (Kjaer, 1958). (Walas, 1988).

17.9. BIOCHEMICAL REACTORS AND PROCESSES

Industrial fermentation is any process involving microorganisms that results in useful products. Among the useful microorganisms are molds, yeasts, algae, and bacteria. They are distinguished from plants and animals by being made of cells of only one kind. Although some kinds are grown as food, yeast or algae, for instance, the main interest here is in chemical manufacture with their assistance. This they accomplish by creating enzymes which catalyze specific reactions. In many respects biochemical processing is like ordinary chemical processing. The recovery and purification of biochemical products, however, often is a more demanding task and offers opportunities for the exercise of ingenuity and the application of techniques that are exotic from the point of view of conventional processing. A distinction also is drawn between processes that involve whole cells and those that utilize their metabolic products, enzymes, as catalysts for further processing. A brief glossary of biochemical terms is in Table 17.22.

Major characteristics of microbial processes are:

- **a.** The reaction medium is aqueous.
- **b.** The products are made in low concentration, rarely more than 5–10% for chemicals and much less for enzyme recovery.
- **c.** Reaction temperatures with microorganisms or isolated enzymes are low, usually in the range of 10–60°C, but the optimum spread in individual cases may be 5°C or less.
- **d.** With only a few exceptions, such as potable ethanol or glucose isomerate, the scale of commercial processes is modest, and for enzymes it is measured only in kilograms per day.
- **e.** Batch processing is used preponderantly, but so many conditions must be regulated carefully that computer control is common.

Because of the small scale of enzyme production, laboratory types of separation and purification operations are often feasible, including: dialysis to remove salts and some low molecular weight substances, ion exchange to remove heavy metals, ultrafiltration with pore sizes under 0.5 μm and pressures of 1–10 atm to remove substances with molecular weights in the range of 15,000–1 million, reverse osmosis to remove water and to concentrate low molecular weight products, and gel permeation chromatography to fractionate a range of high molecular weight substances. Conventional processes of filtration and centrifugation, of drying by freezing or vacuum or spraying, and colloid milling also are used for processing enzymes.

PROCESSING

The three main kinds of fermentation processes are:

- **a.** Growth of microorganisms such as bacteria, fungi, yeasts, and others as end products.
- **b.** Recovery of enzymes from cell metabolism, either intracellularly or as secretions, mostly the latter.
- **c.** Production of relatively low molecular weight substances by enzyme catalysis, either with isolated enzymes or with the whole cell.

Some industrial products of microbial processes are listed in Table 17.23. Chemical and fermentation syntheses sometimes are competitive, for instance, of ethanol, acetone, and butanol.

Enzymes are proteins with molecular weights in the range of 15,000–1,000,000 or so. In 1968, for instance, about 1300 were known, but only a few are of industrial significance. Today there are many more. They are named after the kinds of reactions that

TABLE 17.16. Data for the Overall Heat Transfer Coefficient, u(kcal/m^{2}h°C), in Packed Beds

Authors	Method of Measurement	Heating or Cooling of Gas	Gas	Particles		
				Material	Shape	Diameter D_p, mm
Campbell and Huntington (1952)	Packed bed heat exchanger	H, C	Air, natural gas (82% CH_4)	Glass, alumina, aluminum	Spheres, cylinders	5–25
Chu and Storrow (1952)	″	H	Air	Glass, steel, lead, Socony-Vacuum catalyst beads	Spheres	1–6
Colburn (1931)	″	H	Air	Porcelain, zinc, etc.	Spheres, granules	5–25
Kling (1938b)	″	H	Air	Steel, glass	Spheres	3–4
Leva (1947)	″	H	Air, CO_2	Glass, clay, porcelain	Spheres	3–13
Leva and Grummer (1948)	″	H	Air	Glass, clay, metals, etc.	Spheres, cylinders, granules, etc.	2–25
Leva, Weintraub, Grummer, and Clark (1948)	″	C	Air, CO_2	Glass, porcelain	Spheres	3–13
Leva (1950)	″	H	Air	Glass, clay, porcelain, metal	Spheres, rings, cylinders	4–18
Maeda (1952)	″	C	Air	Catalyst	Cylinders	3–10
Maeda and Kawazoe (1953)	″	C	Air		Granules, rings, saddles	3–25
Verschoor and Schuit (1950)	″	H	Air, H_2	Lead, glass, etc.	Spheres, cylinders, granules	3–10
Tasker (1946)	Phthalic anhydride synthesis	C	Air	Catalyst on quartz (?)	Granules	1.7–2.0

they promote rather than to identify the structure which often is still unknown. Some kinds of enzymes are:

Amylase, which converts polysaccharides (starch or cellulose) to sugars.
Cellulase, which digests cellulose.
Glucose oxidase, which converts glucose to dextrose and levulose.
Isomerase, which converts glucose to fructose.
Lipase, which splits fats to glycerine and fatty acids.
Protease, which breaks down proteins into simpler structures.

Biochemical manufacturing processes consist of the familiar steps of feed preparation, reaction, separation, and purification. The classic mode handles the microorganisms in slurry form in a stirred reactor. Enzyme-catalyzed processes also are performed primarily in stirred tanks, but when the enzymes can be suitably immobilized, that is, attached to solid structures, other kinds of reactor configurations may be preferred. Microbes also are grown in pans or rotating drums under moistened conditions, processes known as solid culture processing. Figure 17.39(a) shows the three modes of microbe culture. Processes that demand extensive handling of moist solids are practiced only on a small scale or when stirred tank action is harmful to cell structures. The process of Figure 17.39(b) consists largely of feed preparation steps.

OPERATING CONDITIONS

The optimum ranges of conditions for microbe growth or enzyme activity are quite narrow and must be controlled closely.

Concentration. A major characteristic of microbial growth and enzymatic conversion processes is low concentrations. The rates of these processes are inhibited by even moderate concentrations of most low molecular weight organic substances, even 1 g/L often being harmful. Nutrients also must be limited, for instance, the following in g/L:

Ammonia	5
Phosphates	10
Nitrates	5
Ethanol	100
Glucose	100

In the fermentation for ethanol, the concentration limit normally is about 8 wt% ethanol, but newer processes have been claimed to

TABLE 17.16.—(*continued*)

Tube		Formula (D_p and D_t in m)	Rage of $N_{Re'}$ or other variable	Remarks
Diameter, D_t, mm	Length L, m			
50–150		$\frac{U}{GC_p} = 0.76\, e^{-0.0225\, a_v Dt}\left(\frac{G}{\mu a_v}\right)^{-0.42}$	30–1000	U refers to tube axis temperature
25	0.3–1.2	$\frac{UD_t}{k_g} = 0.134\left(\frac{D_p}{D_t}\right)^{-1.13}\left(\frac{L}{D_t}\right)^{-0.90}\left(\frac{D_pG}{\mu}\right)^{1.17}$ $\frac{UD_t}{k_g} = 15\left(\frac{D_p}{D_t}\right)^{-0.90}\left(\frac{L}{D_t}\right)^{-0.82}\left(\frac{D_pG}{\mu}\right)^{n}$ $n = 0.55\left(\frac{L}{D_t}\right)^{0.165}$	$\frac{D_tG}{\mu} < 1600$ < 1600 $\frac{D_tG}{\mu} < 3500$	
35–80	0.5–1.2	$U = f\left(\frac{D_p}{D_t}\right) G^{0.83}$	Range of G(kg/m^{2}h): 4500–45000	Function f given in paper. Maximum 0.045 for $\frac{D_p}{D_t} = 0.15$
50	0.3	Graph given in paper	400–3500	
15–52	0.3–0.9	$\frac{UD_t}{K_g} = 0.813\, e^{-6\frac{D_p}{D_t}}\left(\frac{D_pG}{\mu}\right)^{0.90}$	50–3500	
21–52	0.3–0.9		100–4500	Correction factor used for metallic packings
21–52	0.3–0.9	$\frac{UD_p}{K_g} = 3.50\, e^{-4.6\frac{D_p}{\mu}}\left(\frac{D_pG}{\mu}\right)^{0.7}$	150–3000	
15–52	0.3–0.9	$\frac{UD_p}{K_g} = 0.125\left(\frac{D_pG}{\mu}\right)^{0.75}$	500–12000	Correlation valid for high values of $\frac{D_p}{D_t}$
25–100	0.1–0.4	$\frac{UD_t}{K_g} = 4.9\, e^{-2.2\frac{D_p}{D_t}}\left(\frac{D_pG}{\mu}\right)^{0.60}$	100–600	
52–154		See original paper	30–900	Formula varies with shape of material
30–50	0.2–0.3	$\frac{UD_t}{K_g} = 5.783\frac{K_{r,0}}{K_g} + 0.085\left(\frac{D_p}{Dt}\right)^{-0.50}\left(\frac{D_pG}{\mu}\right)^{0.69}$ $+ 0.066\left(\frac{Dt}{L}\right)\left(\frac{Dp}{Dt}\right)^{-1}\left(\frac{D_pG}{\mu}\right)$	40–4000	$K_{r,0}$ is thermal conductivity of bed with stagnant gas
38	0.4–0.7	$U^{-1} = 0.00123 + 0.54G^{-0.83}$	Range of G (kg/m^{2}h): 3000–12000	U refers to tube axis temperature and is corrected for radiation

(Walas, 1988).

function at 10% or so. The search is on for microorganisms, or for creating them, that tolerate high concentrations of reaction products and higher temperatures.

Temperature. Most microbe metabolisms and enzymatic processes function well only in the range of 10–60°C, but in particular cases the active spread of temperatures is only 5–10°C. A classification of microorganisms that is sometimes made is with respect to peak activities near 15°C or near 35°C or near 55°C. The maximum heat effects of metabolic processes can be estimated from heats of formation when the principal chemical participants are known, for instance:

glucose → ethanol, heat of reaction 0.10 kcal/g glucose,
glucose → $CO_2 + H_2O$, heat of reaction 3.74 kcal/g glucose.

Some of the energy is used to form the cell structure. Reactions catalyzed by enzymes may be either endo- or exothermic depending on the particular stoichiometry. Because of the diluteness of the solutions normally handled, temperature control is achieved readily. Stirred fermenters are provided with cooling jackets. Internal cooling oils are undesirable because of the difficulty of cleaning them. Fixed beds of immobilized enzymes do not lend themselves readily to jacket cooling, but in many instances the heat effect is so low that the temperature range can be maintained within the required limits by adjustment of the feed temperature. Multitubular reactors with cooling medium on the shell side are practical with enzymes immobilized on granules.

Sterilization. This is necessary to prevent the growth of foreign microorganisms. Air is sterilized adequately by the heat of compression. Filters at the inlet remove oil and any microbes that may be present, and filters at the air outlet prevent backflow of foreign microorganisms. The inoculum is prepared under sterile conditions in the laboratory. The substrate is sterilized in an external vessel by holding it at 120°C or so for 1 hr or so.

Aeration. Since metabolism of microorganisms is an oxidative process, the substrate should be kept as nearly saturated as possible. At usual fermenter operating conditions the solubility of oxygen is about 0.03 mmol/L. When the content falls to 0.01 mmol/L,

TABLE 17.17. Heat Transfer Coefficient between Particle and Gas

Authors	Method of Measurement	Heating or Cooling of Gas	Gas	Particles		
				Material	Shape	Diameter D_p, mm
Furnas (1930 a, b, c, 1932)	Unsteady heat transfer	H, C	Air, flue gas	Iron ore, limestone, coke, etc.	Granules	4–70
Löf and Hawley (1948)	″	C	Air	Granitic gravel	Granules	8–34
Saunders and Ford (1940)	″	C	Air	Steel, lead, glass	Spheres	1.6–6.4
Tsukhanova and Shapatina (1943), Chukhanov and Shapatina (1946)	″	C	Air	Steel, chamotte, copper	Spheres, cylinders, granules	2–7
Dayton *et al.* (1952)	Cyclic variations		Air	Glass	Spheres	3–6
Glaser (1955)	″		Air	Stoneware	Raschig rings	5–17
Gamson, Thodos, and Hougen (1943)	Drying		Air	Porous celite	Spheres, cylinders	2–19
Wilke and Hougen (1945)	″		Air	Porous celite	Cylinders	2–19
Taecker and Hougen (1949)	″		Air	Porous claykieselguhr	Raschig rings, Berl saddles	6–50
Eichhorn and White (1952)	Dielectrical heating		Air	Plastic	Spheres	0.1–0.7
Satterfield and Resnick (1954)	Decomposition of H_2O_2		Vapors of H_2O and H_2O_2	Catalyst	Spheres	5

(Walas, 1988).

the growth rate falls to about one-half the maximum. Compressed air is introduced through spargers. Dispersion with high-speed agitators rarely is feasible because of possible mechanical destruction of cells. In some sensitive systems, all of the necessary agitation may be provided with an adequate air flow.

Agitation. The purpose of agitation is to keep the microorganisms in suspension, to maintain uniformity to eliminate concentration gradients and hot spots, and to improve heat transfer to the cooling jacket. For the design of agitation systems refer to Chapter 10. In vessels of 1000 gal or more, a power input of about 10 HP/1000 gal and impeller tip speeds of 15–20 ft/sec are adequate, but the standard fermenter described in Table 20.8 is supplied with about four times this power.

pH. Biochemical processes are highly sensitive to hydrogen-ion concentration. Most enzymes function best in the range of pH from 5 to 7, but some extremes are pepsin at pH of 1.5 and

TABLE 17.18. Formulas for the Heat Transfer Coefficient at the Walls of Packed Vessels[a]

Name	Geometry	Formula
1. Beek (1962)	spheres	$\mathrm{Nu} = 0.203\ \mathrm{Re}^{1/3}\ \mathrm{Pr}^{1/3} + 0.220\ \mathrm{Re}^{0.8}\ \mathrm{Pr}^{0.4},\ \mathrm{Re} < 40$
2. Beek (1962)	cylinders	$\mathrm{Nu} = 2.58\ \mathrm{Re}^{1/3}\ \mathrm{Pr}^{1/3} + 0.094\ \mathrm{Re}^{0.8}\ \mathrm{Pr}^{0.4},\ \mathrm{Re} < 40$
3. Yagi-Wakao (1959)	spheres	$\mathrm{Nu} = 0.186\ \mathrm{Re}^{0.8}$
4. Hanratty (1954)	cylinders	$\mathrm{Nu} = 0.95\ \mathrm{Re}^{0.5}$
5. Hawthorn (1968)		$\mathrm{Nu} = 0.28\ \mathrm{Re}^{0.77}\mathrm{Pr}^{0.4}$
6. Doraiswamy and Sharma (1984)	spheres	$\mathrm{Nu} = 0.17\ \mathrm{Re}^{0.79},\ L/d_t > 50,\ 20 < \mathrm{Re} < 7600,\ 0.05 < d_p/d_t < 0.30$
7. Doraiswamy and Sharma (1984)	cylinders	$\mathrm{Nu} = 0.16\ \mathrm{Re}^{0.93},\ L/d_t > 50,\ 20 < \mathrm{Re} < 800,\ 0.03 < d_p/d_t < 0.2$
8. Gnielinski-Martin, Schlünder (1978)		$\mathrm{Nu}/(2.5-1.5\varepsilon) = 0.8[2 + F(\mathrm{Re}/\varepsilon)^{1/2}(\mathrm{Pr})^{1/3}]$
9. Gnielinski-Martin, Schlünder (1978)		$\ln \frac{\mathrm{Nu}}{2.5-1.5\varepsilon} \simeq 0.750 + 0.1061\ \ln(\mathrm{Re}/\varepsilon) + 0.0281[\ln(\mathrm{Re}/\varepsilon)]^2$

[a] Definitions: $\mathrm{Nu} = h_w d_p/k_f$, $\mathrm{Pr} = (C_p\mu/k)_f$, h_w =, wall coefficient, d_p = particle diameter = $6V_p/A_p$, k_f = fluid molecular conductivity, ε = porosity, $\mathrm{Re} = d_pG/\mu$, G = superficial mass velocity per unit cross section.

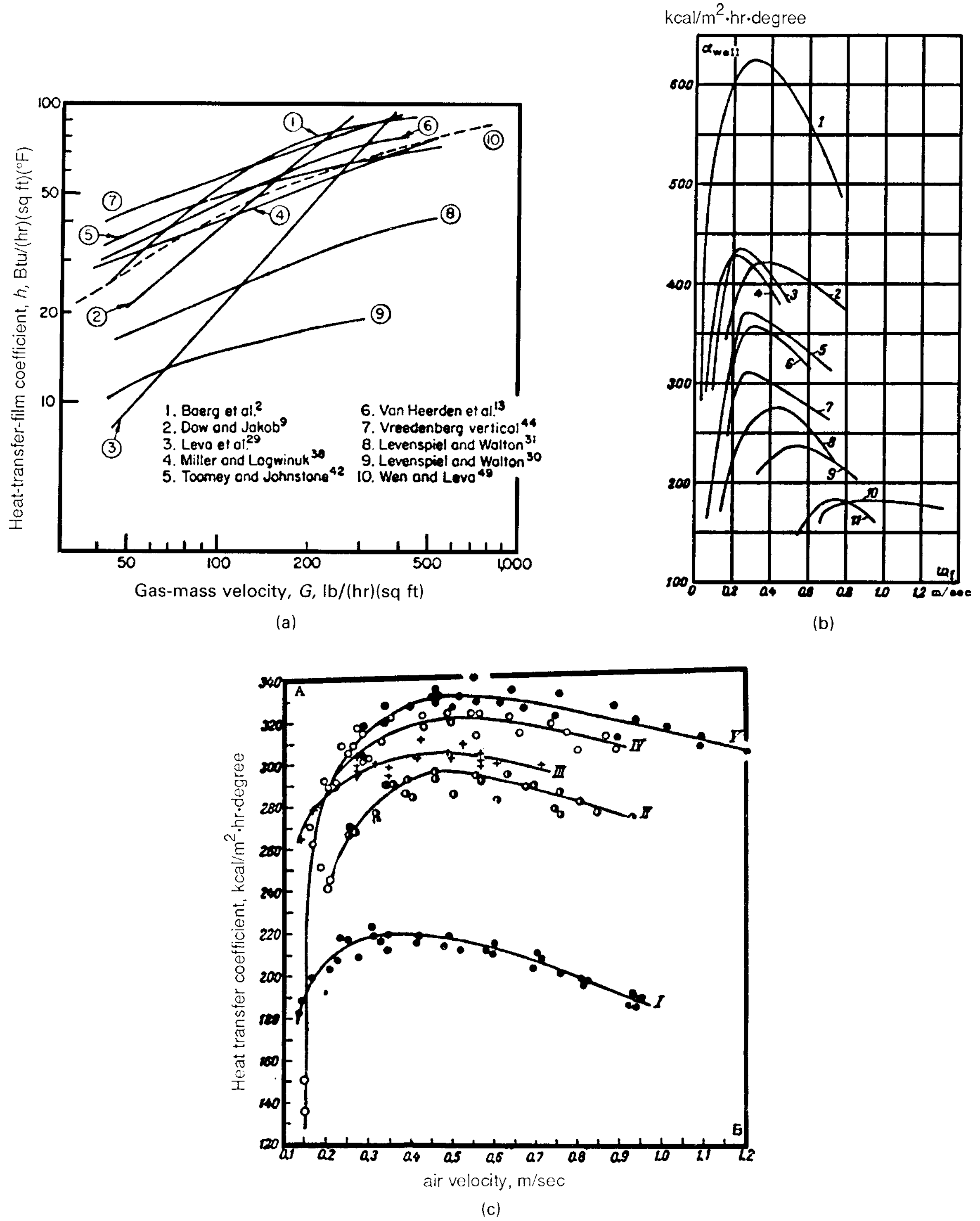
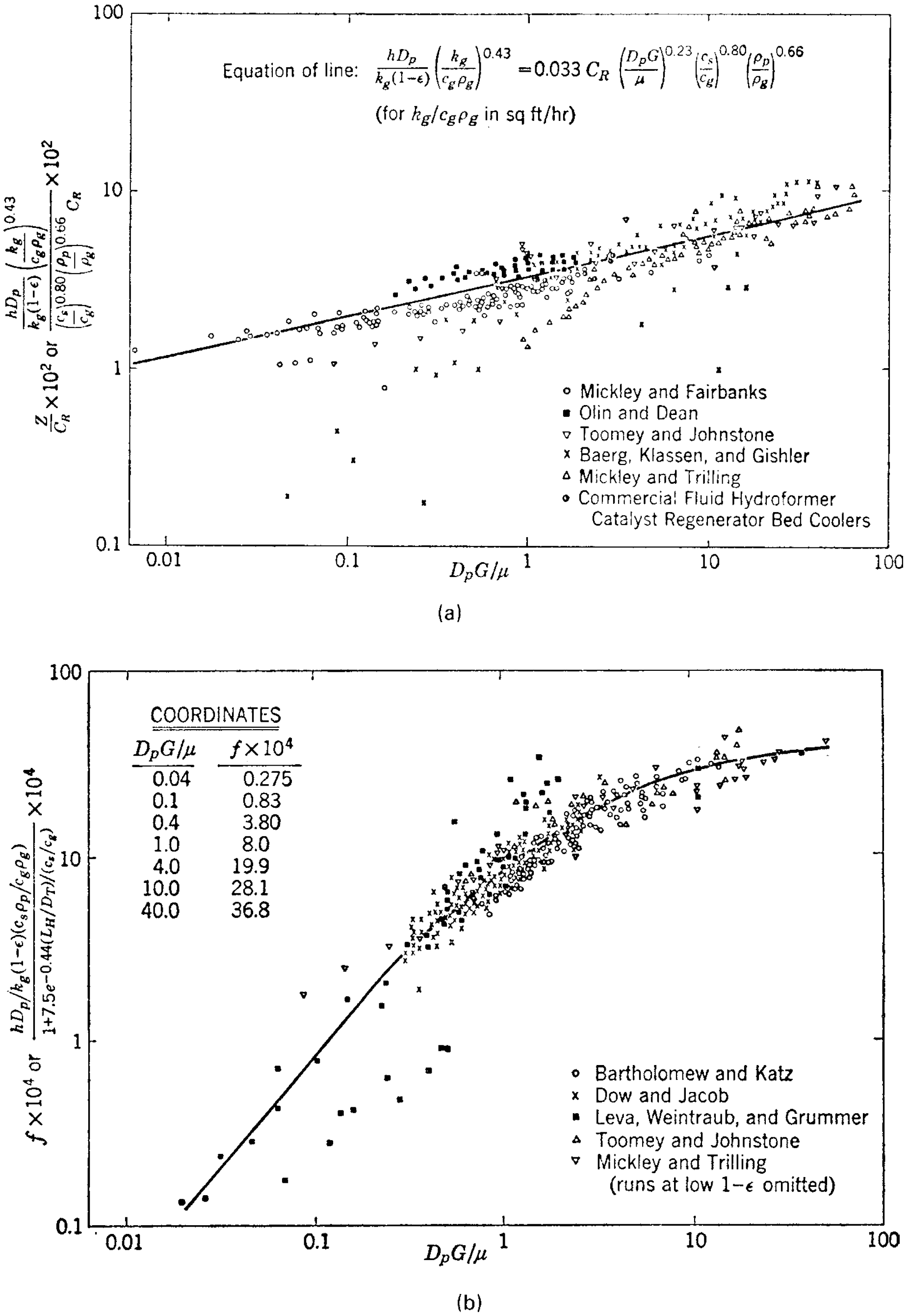


Figure 17.37. Some measured and predicted values of heat transfer coefficients in fluidized beds. 1 Btu/hr(sqft) (°F) = 4.88 kcal/(hr)(m^2) (°C) = 5.678 W/(m^2)(°C). (a) Comparison of correlations for heat transfer from silica sand with particle size 0.15 mm dia fluidized in air. Conditions are identified in Table 17.19 (*Leva, 1959*). (b) Wall heat transfer coefficients as function of the superficial fluid velocity, data of Varygin and Martyushin. Particle sizes in microns: (1) ferrosilicon, d = 82.5; (2) hematite, d = 173; (3) carborundum, d = 137; (4) quartz sand, d = 140; (5) quartz sand, d = 198; (6) quartz sand, d = 216; (7) quartz sand, d = 428; (8) quartz sand, d = 515; (9) quartz sand, d = 650; (10) quartz sand, d = 1110; (11) glass spheres, d = 1160. (*Zabrodsky et al., 1976*, *Fig. 10.17*). (c) Effect of air velocity and particle physical properties on heat transfer between a fluidized bed and a submerged coil. Mean particle diameter 0.38 mm: (I) BAV catalyst; (II) iron-chromium catalyst; (III) silica gel; (IV) quartz; (V) marble (*Zabrodsky et al., 1976*, *Fig. 10.20*). (Walas, 1988).



COORDINATES

D_pG/μ	$f\times 10^4$
0.04	0.275
0.1	0.83
0.4	3.80
1.0	8.0
4.0	19.9
10.0	28.1
40.0	36.8

Figure 17.38. Heat transfer coefficient in fluidized beds. (Wender and Cooper, 1958). (Walas, 1988). (a) Heat transfer at immersed vertical tubes. All groups are dimensionless except $k_g/C_g\rho_g$, which is sqft/hr. The constant CR is given in terms of the fractional distance from the center of the vessel by $C_R = 1 + 3.175(r/R) - 3.188(r/R)^2$. (b) Heat transfer at the wall of a vessel. LH is bed depth, DT is vessel diameter.

TABLE 17.19. Experimental Investigations of Heat Transfer in Fluidized Beds[a]

Reference	Solids	Voidage range	Absolute density, lb per cu ft	Particle-size range, ft	Type of apparatus and operation	Vessel diam., in.	Height of heat-transfer area, in.	Bed height, in.	Fluids	Flow range, lb/(hr)(sq ft)	Temp, °F
1	Sands, graphite, soft brick	Dense phase	83–166	8–14 mesh to 36–72 mesh	Steam-jacketed column	1.5	14.5	………	Air	150–1,200	
2	Iron powder, sands, glass beads catalyst	38.8–75	119–434	0.000198–0.00288	Central electric heat	1.25 in. 5.5	4	10	Air	1.85–605	23.5–65.0
3	Sand, aluminum, calcium carbonate	54–95	160–167	0.000277–0.000822	Wall electric heat	4.0	30	30	Air	96–935	300–450
4	Glass beads	Dilute phase	………	0.00023–0.0036	Electric heat from outside	1.959	12	………	Air	95–3,780	
6	Sand, aluminum, graphite, copper catalyst	Dense phase	24.6–27.2	0.00079–0.0126	Central cooling	2.31	Immersed cooling coil	………	Air	40–100	87–145
9	Aerocat, coke, iron powder	52–69	121–466	0.000363–0.000560	Wall steam heating	2.06 and 3.07	23 and 26.5	2–13	Air	50–300	200–220
13	Carborundum, iron oxide, coke, lead fly ash, alloy	Dense phase	37.5–694	0.000262–0.00213	Wall water cooling	3.4	4	16	Air, CH_4, CO_2, town gas, H_2 and N_2 mixtures	44–779	Approx 10–30°C
17	Glass beads	Dense phase	154	0.00010–0.0011	Internal heating by electric wire	3.0	……….	………	Air, CO_2, Freon-12, He, H_2, H_2 and N_2 mixtures		
26, 29	Sand, iron catalyst, silica gel	35–75	80–500	0.000129–0.00149	Wall steam heat	2.0 and 4.0	25 and 26	12–25	Air, CO_2, He, N_2	1.47–1.095	258–413
30	Coal	Dense phase	………	0.000432–0.00386	Wall cooling (air)	4.0	24	………	Air	50–1,100	
31	Glass beads catalyst, coal	41.7–86.2	63.6–180	0.000250–0.0142	Wall electric heating	4.0	3 sections, 2, 5, and 2 in.	10–30	Air	79–4,350	
36	Glass beads, microspheres	Dense phase	138–153	0.00022–0.00027	Small electric heater probe	………	……….	Approx 18–20	He, air, CH_4, argon	10–150	
37	Glass beads	Dilute phase	151–177	0.000133–0.00149	Internal and external heating	2.875 and 1.00	……….	………	Air	2,700	500
38	Silicon carbide, Al_2O_3, silica gel	Dense phase	70–243	0.000287–0.000817	Center wall cooling	2.0	22	………	Air, He, CO_2	6.4–200	120–414
42	Glass beads	Dense phase	167–179	0.000179–0.00278	Wall water cooling	4.73	7 sections, each 5 in. high	13.2–24.6	Air	23.7–1,542	
43, 44	Sand, iron ore	Dense phase	165–330	0.000766–0.00197	Internal cooling	1.35 in. 22.2	……….	47, 68	Air	65–300	Approx 100–400
50	Carborundum sand, aluminum powder, lead powder, glass beads	Dense phase	160–700	0.00020–0.010	Internal heating by small cylindrical element	3.94	……….	………	Air, CO_2, H_2		

[a] Another list of 29 sources is given by Zabrodsky (1966). (Leva, 1959). (Walas, 1988).

TABLE 17.20. Heat Transfer Coefficients in Fluidized Beds[a]

1. *At vertical tubes* (Vreedenburg, 1960):

$$[h(D-d_t)/k_g](d_t/D)^{1/3}(k_g/C_s\mu_g)^{1/2} = C[u(D-d_t)\rho_s/\mu_g]^n$$

Conditions:

$\rho_s d_s u/\mu_g < 2050$,

$$\begin{cases} \rho_s u(D-d_t)/\mu_g < 2.4\times10^5, C = 2.7\times10^{-16}, n = 3.4 \\ \rho_s u(D-d_t)/\mu_g > 2.4\times10^5, C = 2.2, n = 0.44 \end{cases}$$

$$[h(D-d_t)/k_g](d_t d_s k_g/[(D-d_t)C_s\mu_g]^{1/3} = C[u(D-d_t)g^{0.5}d_s^{1.5}]^n$$

Conditions:

$\rho_s d_s u/\mu_g > 2550$,

$$\begin{cases} u(D-d_t)g^{0.5}{d_s}^{1.5} < 1070, C = 1.05\times10^{-4}, n = 2.0 \\ u(D-d_t)g^{0.5}{d_s}^{1.5} > 1070, C = 240, n = 0.8 \end{cases}$$

For off-center locations, the factor C is multiplied by C_R which is given in terms of the fractional distance from the center by

$$C_R = 1 + 3.175(r/R) - 3.188(r/R)^2$$

2. *At vertical tubes*, see the correlation of Wender and Cooper on Figure 17.17(a)
3. *At horizontal tubes* (Vreedenburg, *loc. cit.*; Andeen and Glicksman, ASME Paper 76-HT-67, 1976):

$$(hd_t/k_g)(k_g/C_s\mu_g)^{0.3} = 0.66[\rho_s d_t u(1-\varepsilon)/\mu_g\varepsilon]^{0.44}, \quad \rho_s d_s u/\mu_g < 2500$$

$$(hd_r/k_g)(k_g/C_s\mu_g)^{0.3} = 900(1-\varepsilon)(d_r u\mu_g/d_s^3\rho_s g)^{0.326}, \quad \rho_s d_s u/\mu_g > 2550$$

4. *At vessel walls*, see Figure 17.17(b) for the correlation of Wender and Cooper.

[a] Notation: Subscript s for solid, subscript g for gas, d_t = tube diameter, D = vessel diameter, g = acceleration of gravity. (Walas, 1988).

TABLE 17.21. Examples of Industrial Gas-Liquid-Solid Reaction Processes

A. Fixed-bed reactors
1. Trickle beds (downflow)
    a. Catalytic hydrodesulfurization, hydrocracking and hydrogenation
    b. Butynediol from acetylene and aqueous formaldehyde
    c. Sorbitol from glycerol
    d. Oxidation of SO_2 in the presence of activated carbon
    e. Hydrogenation of aniline to cyclohexylaniline
2. Upflow (bubble) reactors
    a. Coal liquefaction by SYNTHOIL process
    b. Fischer-Tropsch process
    b. Selective hydrogenation of phenylacetylene and styrene

B. Suspended solid reactors
1. Stirred tanks
    a. Catalytic hydrogenation of fats and oils 17.37, 17.38
    b. Hydrogenation of acetone and nitrocaprolactam
    c. Aerated fermentation with cellular enzymes
    d. Reaction between methanol and hydrogen chloride with $ZnCl_2$ catalyst

2. Slurry towers
    a. Fischer-Tropsch process
    b. Hydrogenation of methyl styrene and carboxy acids
    c. Oxidation and hydration of olefins
    d. Polymerization of ethylene
    e. Calcium hydrophosphite from white phosphorous and lime slurry
    f. Lime/limestone process for removal of SO_2 from flue gases

3. Fluidized bed of catalyst
    a. Calcium acid sulfite from $CaCO_3 + SO_2 + H_2O$
    b. Coal liquefaction
    c. Hydrocracking and hydrodesulfurization

TABLE 17.22. A Biochemical Glossary

Microorganisms (microbes) are living cells, single or in multiples of the same kind, including bacteria, yeasts, fungi, molds, algae and protozoa. Their metabolic products may be of simple or complex structure.

Fermentation is a metabolic process whereby microorganisms grow in the presence of nutrients and oxygen, sometimes in the absence of oxygen. The terms used are aerobic (in the presence of oxygen) and anaerobic (in the absence of oxygen).

Substrate consists of the nutrients on which a microorganism subsists or the chemicals upon which an enzyme acts.

Enzymes are made by living cells, and are proteins with molecular weights ranging from about 15,000 to 1,000,000. They are able to catalyze specific reactions.

Enzymes, immobilized, are attached to a solid support by adsorption or chemical binding or mechanical entrapment in the pores of a gel structure, yet retain most of their catalytic powers.

-*ase* is a suffix identifying that the substance is an enzyme. The main part of the name describes the nature of the chemical reaction that can be catalyzed, as in cellulase, an enzyme that catalyzes the decomposition of cellulose.

araginase at pH of 10. For classes of microorganisms, these ranges are common:

Complex cells	6.5–7.5
Bacteria	4–8
Molds	3–7
Yeasts	3–6

Control of pH is accomplished by additions of dilute acid or alkali.

Ion Concentration. Heavy metals, particularly calcium, inhibit enzyme activity. The only feasible method of removing them is with ion exchange resins.

Foam Control. Fermentations tend to froth because metabolites have surfactant properties. Prevention commonly is by addition of antifoam agents such as oils, heavy alcohols, fatty acids, or silicones. High-speed rotating impellers destroy bubbles by direct impact and by throwing them against the wall of the vessel.

REACTORS

Stirred tanks are the chief kind of reactors for handling microorganisms or dissolved isolated enzymes, either as batch units or as continuous stirred tank batteries. When the enzymes are immobilized, a variety of reactor configurations is possible and continuous operation is easily implemented. The immobilization may be on granules or on sheets, and has the further advantage of making the enzymes reusable since recovery of dissolved enzymes rarely is feasible.

Many aspects of the design of biochemical reactors are like those of ordinary chemical reactors. The information needed for design are the kinetic data and the dependence of enzyme activity on time and temperature. Many such data are available in the literature, but usually a plant design is based on laboratory data obtained with small fermenters. Standard sizes of such units range from 50 to 1000 L capacity.

A sketch of a plant size fermenter and some of its auxiliaries is in Figure 17.40. Although not shown here, a bottom drive mechanical agitator usually is provided. The standard specification, Table 17.24, of one make of commercial fermenter includes a listing of the many openings that are required, as well as other general information.

The major disadvantages of large-scale equipment is as the volume increases, the surface to volume ratio decreases, circulation time of contents increases and the corresponding mixing intensity decreases. In large vessels, the reactions tend to slow down that otherwise might be fast. Further, large volume conventional stirred tank and packed bed reactors tend to be inefficient with lower yield as well as producing more impurities or by-products.

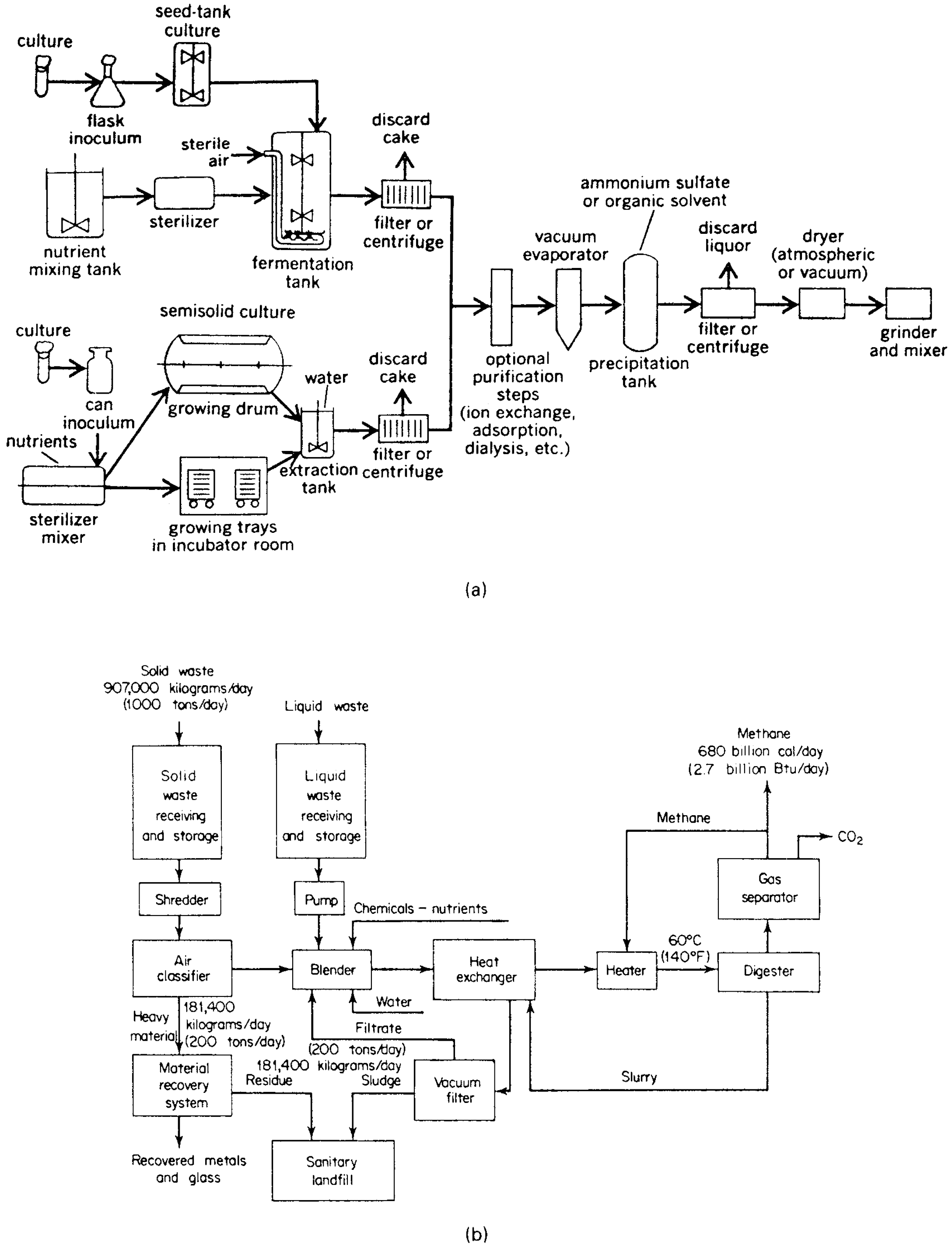
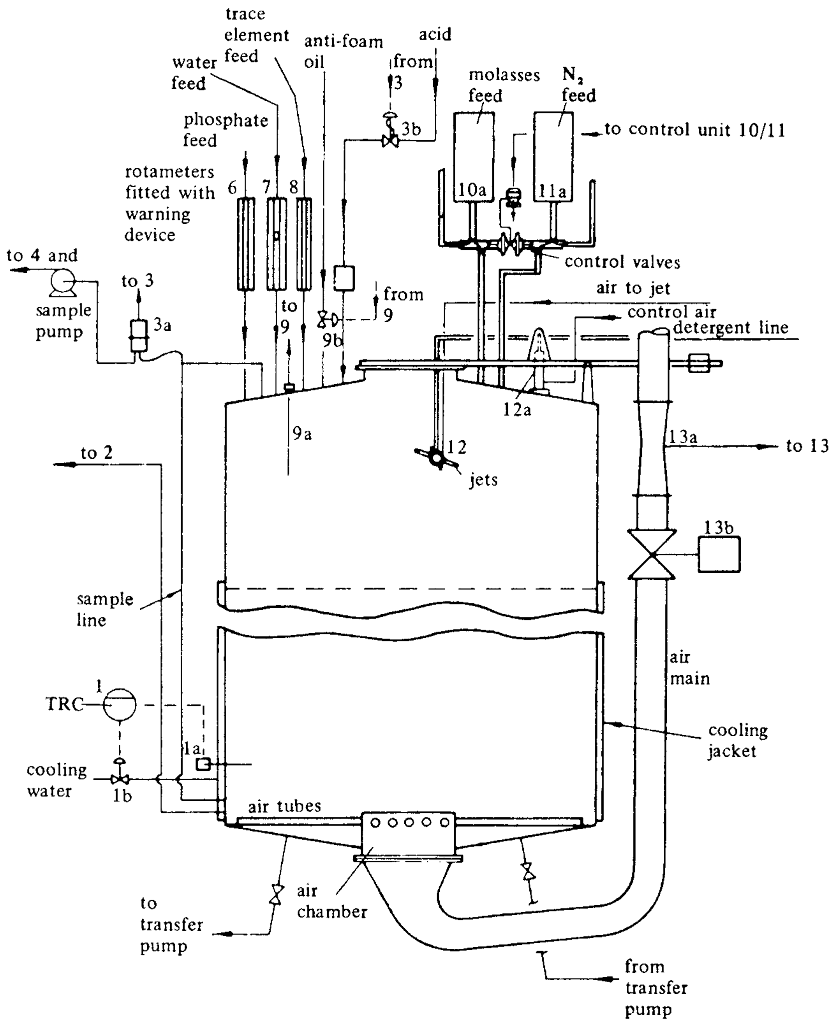


Figure 17.39. Flowsketches of two processes employing fermentation. (a) Process for enzyme production, showing the use of growing trays, growing drums, and stirred tank. Purification steps are the same for all three modes of culture growth. (b) Production of methane-rich gas by anaerobic digestion of finely divided waste solids in a 10–20% slurry. Residence time in the digester is five days. (Considine, 1977).



*1	Temperature controller and recorder
1a	Resistance thermometer
1b	Control valve
*2	Fermenter level
*3	pH recorder and controller
3a	pH electrode system
3b	Control valve
*4	Yeast concentration recorder
*5	Recorder controller
6	Phosphate feed rotameter
7	Water feed rotameter
8	Trace element feed rotameter
*9	Foam controller
9a	Foam detector
9b	Control valve
10/11	Dosage control unit
10a	Molasses feed
11a	Nitrogen feed
12	Rotor jet
12a	Power unit
*13	Air controller recorder
13a	Venturi
13b	Power operated air control valve

*Indicates panel-mounted instruments.

Figure 17.40. Sketch of a fermenter with its auxiliary equipment. In most cases supplemental agitation by mechanical stirrers is common. (*Olsen*, Chem. Ind., *416, 1960*).

TABLE 17.23. Industrial Products of Microbial and Related Processes

A. Significant or marginal products
- Acetic acid
- Amino acids
- Butyric acid
- Citric acid
- Ethanol
- Fructose from glucose
- Glucose from starch
- Gluconic acid
- Methane
- Nucleotides (glutamic acid, guanyl acid, xanthyllic acid)

B. Products under development or absolesced from microbial synthesis
- Acids: fumaric, lactic, malic, oxalic and some others
- Acetone
- Butanol
- Butanediol
- Glycerine
- Lipids
- Polyalcohols and other substances

C. Enzymes (extensive lists with properties and industrial suppliers are in the book by Godfrey and Reichelt, 1983).

D. Antibiotics (Lists with major characteristics, sources and manufacturing methods are in, for example, the book of Bailey and Ollis, 1986).

TABLE 17.24. Standard Specifications of a Fermenter

1. Surfaces in contact with culture are 316 SS, all others 304 SS; free of crevices, mechanically ground and polished to approx 220 grit
2. Approx proportions: height/diameter = 2, impeller/vessel diameter = 0:35, baffle width/vessel diameter = 0:1
3. Maximum working volume = 75–80%, minimum = 25%
4. Ports and penetrations are 20 in number, namely
   - **A.** Steam-sterilizable inoculation/addition port
   - **B.** Combination viewing window/filling port on headplate
   - **C.** Light entrance window and lamp on headplate
   - **D.** Air inlet line
   - **E.** Air exhaust line
   - **F.** Well for temperature control sensor and temperature recorder sensor
   - **G.** Well for thermometer
   - **H.** Water inlet line to jacket of vessel
   - **I.** Water outlet line from jacket of vessel
   - **J.** Rupture disc on headplate and pressure relief valve on jacket
   - **K.** Diaphragm-type pressure gauge
   - **L.** Steam-sterilizable sample port
   - **M.** Steam-sterilizable bottom drain port, discharge valve is flush-bottom
   - **N.** Side-entry port for pH electrode
   - **O.** Top-entering or side-entering (size-dependent) port for installation of the dissolved oxygen electrode
   - **P.** Top-entering port for foam sensor
   - **Q.** Side-entering ports for acid, base, and antifoam addition (valved and piped as required)
   - **R.** Spare penetrations on headplate for insertion of additional sensors i.e., 1 1/8 in. NPT, 1 3/8 in. NPT, 1 3/4 in. NPT
5. Foam breaking: Injection port provided for chemical breaking; mechanical breaker optional, consists of a double disk rotated at high speed with its own drive
6. Agitation system has three six-bladed turbine impellers adjustable along the shaft, maximum tip speed of 1200 ft/min, standard drive of 40 HP for a 5000-L vessel, bottom drive standard, top drive optional
7. Controls and monitors: liquid level, pH, dissolved oxygen, reduction–oxidation (Redox) potential, air rate, temperature, optional automatic sterilization cycle control, rupture disk on vessel, relief valve on jacket

(New Brunswick Scientific Co.).

The advantages of small-scale reactors are overcoming mass-transfer and heat transfer resistances, increased surface-to-volume ratios, decreased mixing times, etc. Although microreactors have numerous advantages over large-scale reactors, a number of such units would have to be combined so that commercial-scale production rate can be achieved. As the design and performance of these small-scale reactors are studied and become better understood, design engineers will recognize their advantages and new designs will be forthcoming.

For the present, to achieve satisfactory production rates, biochemical reactions are carried out industrially in classical chemical reactors like those shown in Figure 17.40.

Doble (2008) presented a number of potential biochemical equipment designs, most of which are of laboratory scale. A sampling follows:

Loop reactor
Oscillatory flow mixing reactor
Plate reactor with heat exchanger
Endo/exo catalytic plate reactor
Endo/exo catalytic annular tube reactor
Tube-inside-a-tube reactor
Rotating packed bed contactor
Rotating catalytic basket reactor
Spinning disc reactor

These microreactors may be fabricated from various materials such as quartz, silicon, metals, polymers, ceramics and glass.

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