Chapter 9

Unit Operations and Pollution Prevention

Contents

9.1 Introduction

In developing a flowsheet for the production of a chemical, it is desirable to consider the environmental ramification of each unit operation in the process rather than postponing this consideration until the flowsheet is finished. This “front end” environmental assessment is more likely to result in a chemical process that has less potential to cause environmental harm.

In many instances, this environmentally benign design will also be more profitable, because the improved design will require lower waste treatment and environmental compliance costs and will convert a higher percentage of raw materials into salable product.

ramification: 결과

9.1 Introduction

In considering pollution prevention for unit operations in the design of chemical processes, the following considerations are important.

- **Front-End Pollution Prevention Considerations**.

1. **Material Selections**
2. **Waste Generation Mechanisms**
3. **Operation Conditions**
4. **Material Storage and Transfer**
5. **Energy consumption**
6. **Process Safety**

9.1 Introduction

1. **Material Selections:** Many of the environmental concerns can be addressed by reviewing materials properties and making correct choice of unit operation & conditions. The materials used in each unit operation should be carefully considered so as to minimize the human impact and environmental damages of any releases that might occur.

2. **Waste Generation Mechanisms:** Often, a careful evaluation of the mechanisms of in-process waste generation can direct the process designer toward environmentally sound material choices and other pollution prevention options.

3. **Operation Conditions:** The operating conditions of each unit should be optimized in order to achieve maximum reactor conversion and separation efficiencies

9.1 Introduction

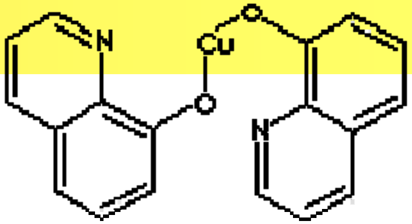
4. **Material Storage and Transfer:** The best material storage and transfer technologies should be considered in order to minimize releases of materials to environmental.

5. **Energy consumption:** Energy consumption in each unit should be carefully reviewed so as to reasonably minimize its use and the associated release of utility-related emissions.

6. **Process Safety:** The safety ramifications of pollution prevention measures need to be reviewed in order to maintain safe working conditions.

In following sections, we apply this framework for preventing pollution in unit operations by considering choices in materials, technology selection, energy consumption, and safety ramifications.

9.1 Introduction



"RISK SHIFTING 1"

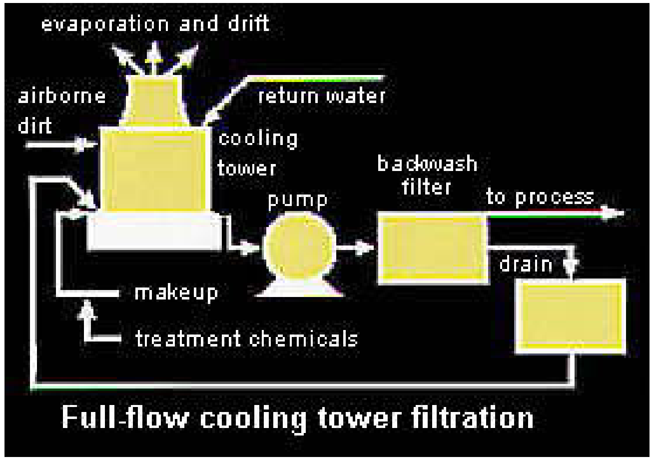
Pollution prevention decisions that are targeted to reduce one kind of risk may increase the level of risk in other areas. For example, a common method of conserving water resources at chemical manufacturing facilities is employ cooling towers. Process water used for cooling purposes can be recycled and reused many times.

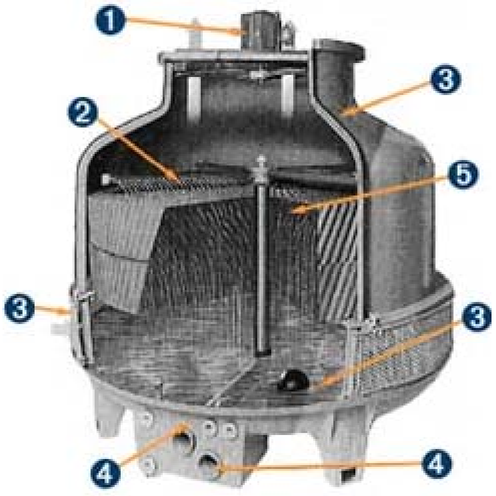
However, there is an increased risk for workers who may exposed to the biocide used to control microbial growth in the cooling water circuit (anti-fungal biocide, e.g., copper-8-quinolinolate).

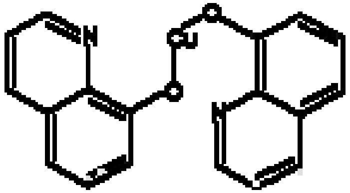
Also, in some cooling water processes, hazardous waste is created by the accumulation of solids: for example, from the use of hexavalent chromium (a cancer causing agent) as a corrosion inhibitor.

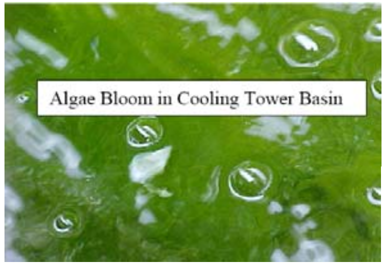
Cooling tower

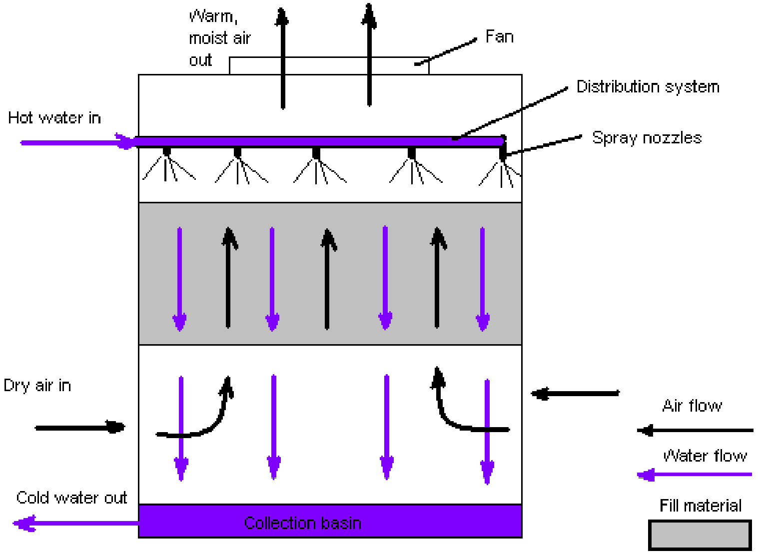
cooling towers











Counterflow type design

9.1 Introduction

“RISK SHIFTING 2”

Another example of shifting risk from the environment and the general population to workers involves fugitive sources (valves, pumps, pipe connectors, etc.).

One strategy for decreasing fugitive emissions is reduce the number of these units by eliminating backup units and redundancy. This strategy will decrease routine air releases but will increase the probability of catastrophic release or other safety incidents.

Simply put, the objective of pollution prevention is to reduce the overall level of risk in all areas and not to shift from one type to another.

9.2 Pollution Prevention in Material Selection for Unit Operations

One important element of designing and modifying process units for pollution prevention is *the choice of materials* that are used in chemical processes. These materials are used as feedstocks, solvents, reactants, mass separation agents, diluents, and fuels.

In considering their suitability as process components, it is not sufficient to consider only material properties that are directly related to processing; it is increasingly important to consider the environmental and safety properties as well.

Use of materials that are known to be persistent, bioaccumulative, or toxic should be avoided as they are under increasing regulatory scrutiny and many manufactures are moving away from their use.

9.2 Pollution Prevention in Material Selection for Unit Operations

Questions regarding material selection include:

a) What are the environmental, toxicological, and safety properties of the material ?

b) How do these properties compare to alternative choices ?

c) To what extent does the material contribute to waste generation or emission release in the process ?

d) Are there alternative choices that generate less waste or emit less while maintaining or enhancing the overall yield of the desired product ?

If processing materials can be found which generate less waste and if the hazardous characteristics of those wastes are less problematic, then significant progress may be made in preventing pollution from the chemical process.

9.2 Pollution Prevention in Material Selection for Unit Operations

Materials are involved in a wide range of processing functions in chemical manufacturing, and depending on the specific application, their environmental impacts vary greatly.

For example, ***reactants*** for producing a particular chemical can vary significantly with respect to toxicity and inherent environmental impact potential (global warming, ozone depletion, etc.,), and they can exhibit various degrees of selectivity and yield toward the desired product. In addition, the properties of reaction byproducts can vary widely, similarly to reactants.

9.2 Pollution Prevention in Material Selection for Unit Operations

Some ***catalysts*** are composed of hazardous materials or they may react to form hazardous substances. For example, catalysts used for hydrogenation of carbon monoxide can form volatile metal carbonyl compounds, such as nickel carbonyl, that are highly toxic.

Many catalysts contain heavy metals, and environmentally safe disposal has become an increasing concern and expense. After the deposition of inhibitory substances, the regeneration of certain heterogeneous catalysts releases significantly amounts of SO_x, NO_x, and PM. For example, the regenerator for a fluid catalytic cracking unit (FCCU) is a major source of air pollution at refineries. Note that the removal of the FCCU would result in very low yields and consequently unacceptable waste generation at facility level.

9.2 Pollution Prevention in Material Selection for Unit Operations

The choice of a mass separating agent for solids leaching or liquid extraction applications can affect the environmental impacts of those unit operations. Agents that are matched well to the desired separation will consume less energy and release less energy-related pollutants than those that are not well suited for the application. Typically, agents that have lower toxicity will require less stringent clean up levels for any waste streams that are generated in the process.

The choice of fuel for combustion in industrial boilers will determine the degree of air pollution abatement needed to meet environmental regulations for those waste streams. As an illustration, using fuel types having lower sulfur, nitrogen, and trace metals levels will yield a flue gas with lower concentrations of acid rain precursors (SO_x and NO_x) and particulate matter.

9.2 Pollution Prevention in Material Selection for Unit Operations

Example 9.2-1 : Compare the emission of SO_2 resulting from the combustion of three fuel types that will satisfy an energy demand of 10^6 BTU.

	No. 6 F.O.	No. 2 F.O.	Natural Gas
Density (lb/ft^3)	61.23	53.66	0.0485
Heating Value (BTU/gal)	148,000	130,000	1060 BTU/ft^3
Carbon (wt%)	87.27	87.30	74.8
Hydrogen (wt%)	10.49	12.60	25.23
Sulfur (wt%)	0.84	0.22	0
Oxygen (wt%)	0.64	0.04	0.0073
Nitrogen (wt%)	0.28	0.006	
Ash (wt%)	0.04	<0.01	

No. 6 F.O.

10^6 BTU/148,000 BTU/gal=6.76 gal = 55.34 lb

SO_2 generated = (55.34 lb)(0.0084 lb S/lb)(64.06 lb SO_2/32.06 lb S)=0.929 lb SO_2

No. 2 F.O.

10^6 BTU/130,000 BTU/gal=7.69 gal = 62.95 lb

SO_2 generated = (62.95 lb)(0.0022 lb S/lb)(64.06 lb SO_2/32.06 lb S)=0.276 lb SO_2

Natural Gas

SO_2 generated = 0.0 lb

9.2 Pollution Prevention in Material Selection for Unit Operations

Less toxic materials, such as water and air, can still have important environmental implications due to the waste streams that are generated in their use.

Air is often used in chemical reactions either as a diluent or as a source of oxygen. For certain high temperature reactions, the N_2 and O_2 molecules in the air react, forming oxides of nitrogen. Upon release, NO_x will participate in photochemical smog reactions in the lower atmosphere. Therefore, it is important to consider alternative sources of oxidants, such as enriched air or pure oxygen, and diluents, such as CO_2 or other inert reaction byproducts.

Water is used for many purposes in chemical processes; as boiler feed, a cooling medium, reactant, or a mass separating agent. The following example illustrates that the quality of the feed water can have a profound influence on the generation of hazardous waste in a refinery

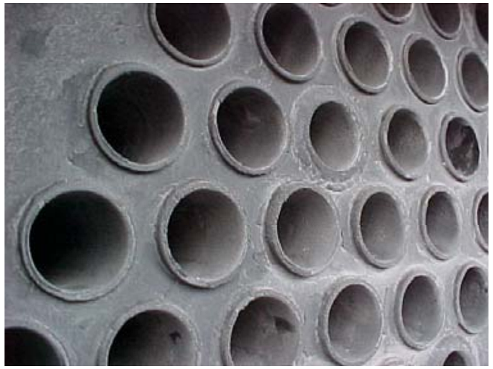
9.2 Pollution Prevention in Material Selection for Unit Operations

Example 9.2-2

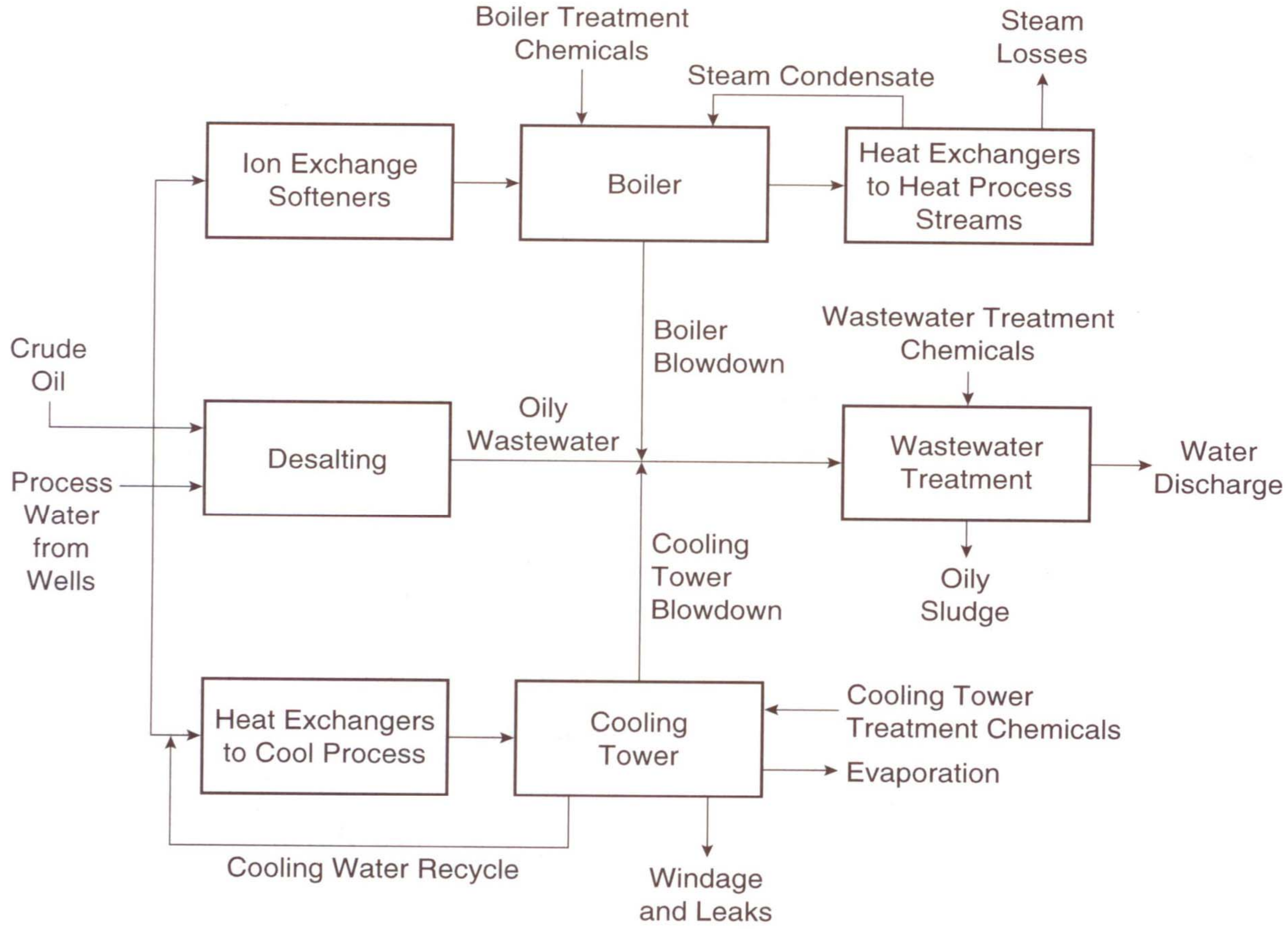
Solid accumulate in the boiler and excessive levels of suspended solids lead to fouling of heat transfer surfaces in the process, a decrease in heat transfer efficiency, and requires periodic shut-down and cleaning of these surfaces to restore normal operation.

To control solids accumulation, the content of the boiler are sent to wastewater treatment when the dissolved solids content is above a cut-off level, in a step termed “blow-down”

Use all process water using RO to separate dissolved solids !



9.2 Pollution Prevention in Material Selection for Unit Operations



9.3 Pollution Prevention for Chemical reactors

- From an environmental perspective, reactors are the most important unit operation in a chemical process

- Degree of conversion of feed to desired products influences
  - ~ all subsequent separation processes,
  - ~ recycle structure for reactors,
  - ~ waste treatment options,
  - ~ energy consumption, and
  - ~ ultimate pollutant releases to the environment.

- Reactor considerations with pollution prevention idea:
  1) material use and selection
  2) reaction type and reactor choice, and
  3) reactor operation

(Table 9.2-1)

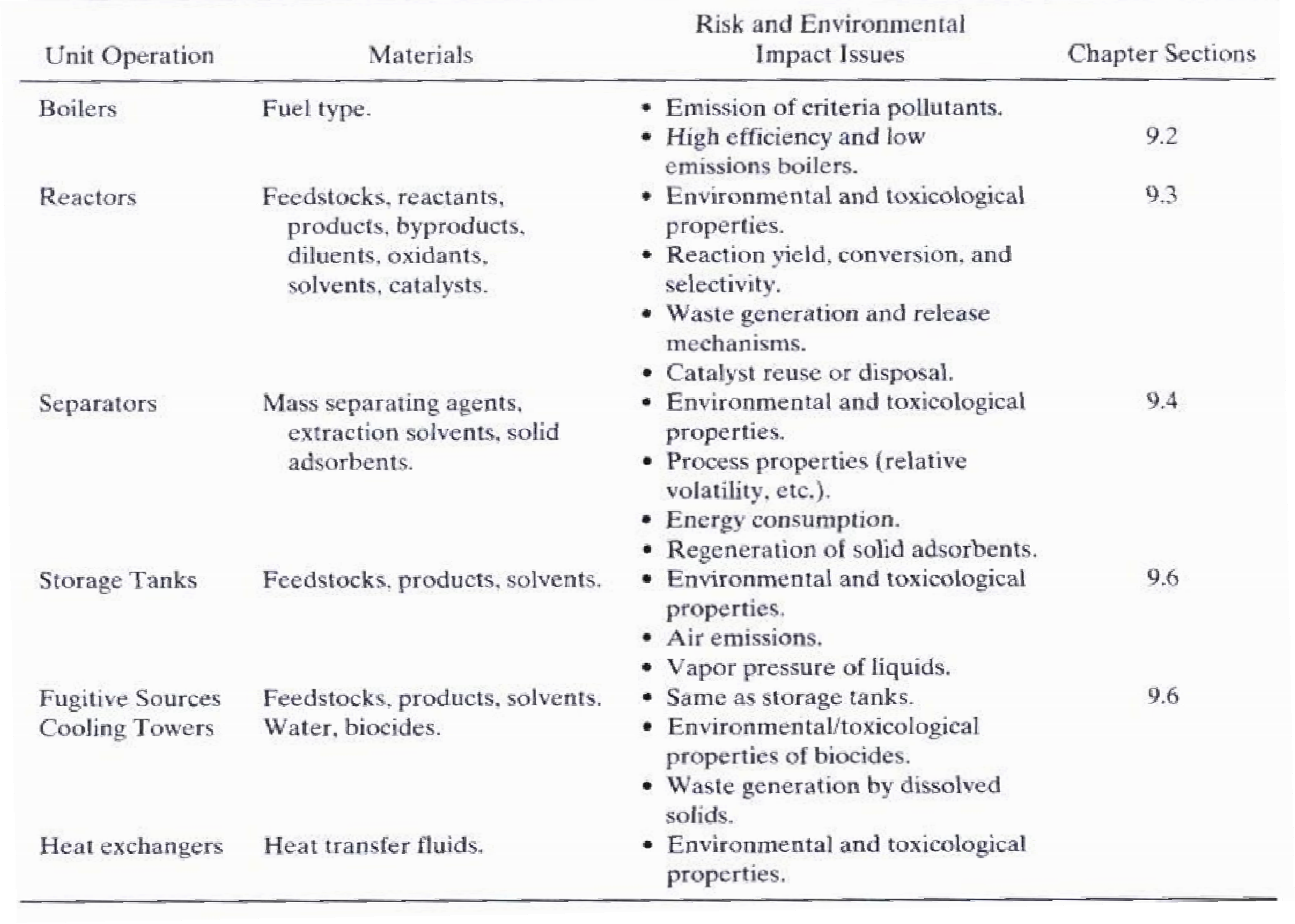
Material Use and Selection for Reactors

Issues involving the use of materials in the light of their influence on environmental impact of reactors

- raw materials and feedstocks
- catalyst
- solvent, diluents, etc.

Table 9.2-1

Summary of material selection issues for unit operations in chemical processes



Unit Operation	Materials	Risk and Environmental Impact Issues	Chapter Sections
Boilers	Fuel type.	• Emission of criteria pollutants. • *High efficiency and low emissions boilers.*	9.2
Reactors	Feedstocks, reactants, products, byproducts, diluents, oxidants, solvents, catalysts.	• Environmental and toxicological properties. • Reaction yield, conversion, and selectivity. • Waste generation and release mechanisms. • Catalyst reuse or disposal.	9.3
Separators	Mass separating agents, extraction solvents, solid adsorbents.	• Environmental and toxicological properties. • Process properties (relative volatility, etc.). • Energy consumption. • Regeneration of solid adsorbents.	9.4
Storage Tanks	Feedstocks, products, solvents.	• Environmental and toxicological properties. • Air emissions. • Vapor pressure of liquids.	9.6
Fugitive Sources	Feedstocks, products, solvents.	• Same as storage tanks.	9.6
Cooling Towers	Water, biocides.	• Environmental/toxicological properties of biocides. • Waste generation by dissolved solids.	
Heat exchangers	Heat transfer fluids.	• Environmental and toxicological properties.	

Raw Materials and Feedstocks

- Raw materials can be highly toxic or cause undesirable byproducts and their presence be a concern of the uncontrolled release and exposure to humans (eliminate as many of these toxic raw materials, intermediates and products as possible)

- May necessitate the adoption of new process chemistry (Phosgene free process for polycarbonates)

- In the production of fuels for transportation, petroleum refineries are required to remove sulfur from products (if not, SO_2 is releases to air and damage ecosystems)

- In partial oxidation of hydrocarbons and air is the source of O_2 that produce NO_x (precursors of smog)

Solvents

- Most solution and emulsion polymerization requires solvents (enhance reactions, co-solubilize monomers, diluting medium to modulate reactions)

- Substitution of environmentally-benign solvents (in terms of solubility, toxicological, cost, environmental properties)

- Supercritical Fluids

Catalysts

- Catalysts are either homogeneous or heterogeneous (choice has large impact on the efficiency of the reactor and environment)

- Catalysts can allow the use of more environmentally-benign chemicals as raw materials

- Catalysts can increase selectivity toward the desired product and away from unwanted byproducts (waste)

- They can convert waste chemicals to raw materials and create more environmentally acceptable products directly from reactions

Catalysts

Example:

Production of reformulated gasoline (RFG) and diesel fuels from crude oil

How improved catalyst can create chemicals that are better for environment

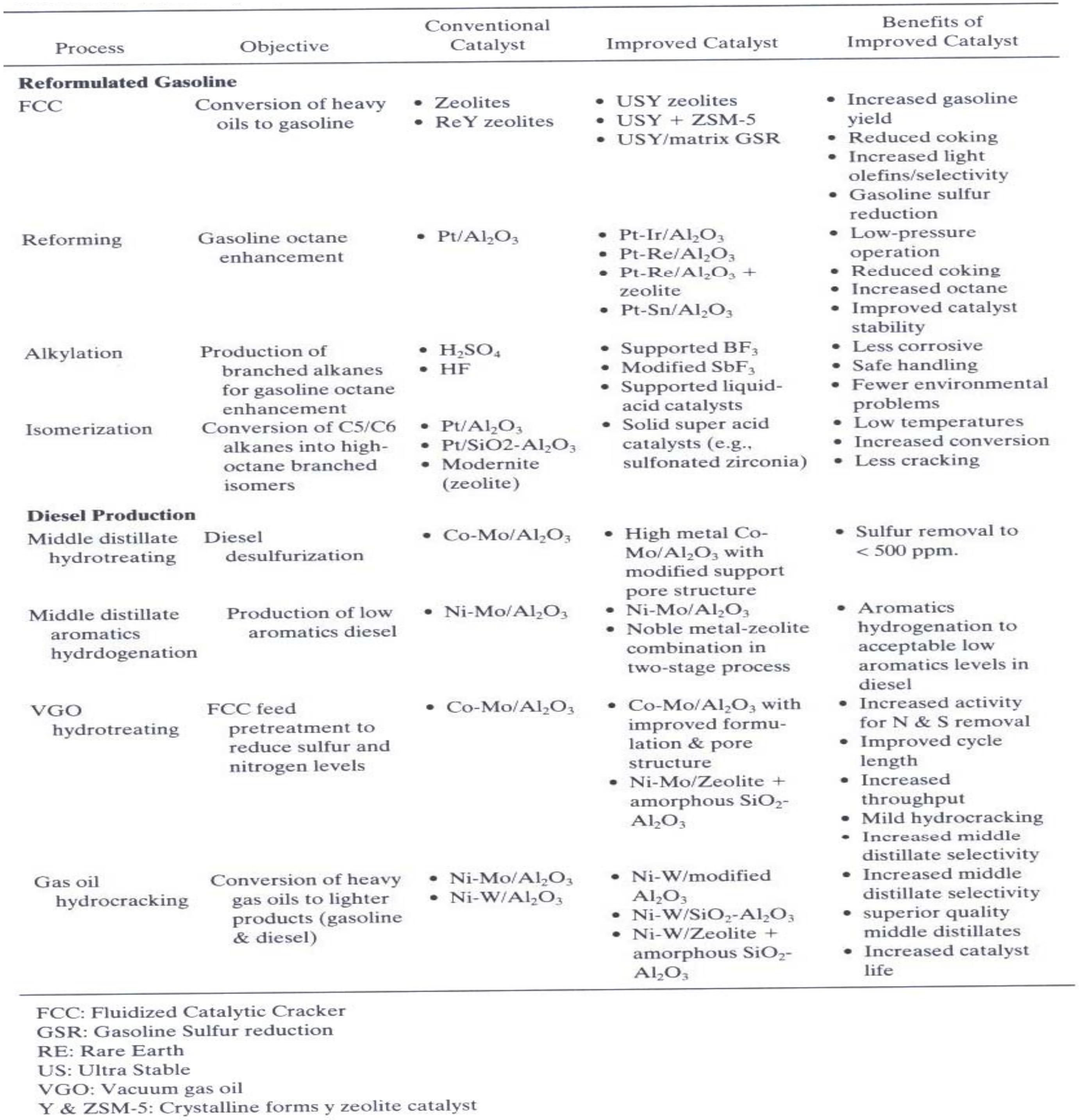
Trends:

a) increased processing of crude oils with lower quality
(higher % of sulfur, N, metals and carbon residues)
b) more demand of lighter fuels and less for heavy oils
c) environmental regulations that limit % of sulfur, heavy metals, aromatics, VOC in transportation fuels

(Table 9.3-1)

Table 9.3-1

Summary of conventional and improved catalysts for reformulated gasoline and diesel production



Process	Objective	Conventional Catalyst	Improved Catalyst	Benefits of Improved Catalyst
Reformulated Gasoline				
FCC	Conversion of heavy oils to gasoline	• Zeolites • ReY zeolites	• USY zeolites • USY + ZSM-5 • USY/matrix GSR	• Increased gasoline yield • Reduced coking • Increased light olefins/selectivity • Gasoline sulfur reduction
Reforming	Gasoline octane enhancement	• Pt/Al_2O_3	• $Pt\text{-}Ir/Al_2O_3$ • $Pt\text{-}Re/Al_2O_3$ • $Pt\text{-}Re/Al_2O_3$ + zeolite • $Pt\text{-}Sn/Al_2O_3$	• Low-pressure operation • Reduced coking • Increased octane • Improved catalyst stability
Alkylation	Production of branched alkanes for gasoline octane enhancement	• H_2SO_4 • HF	• Supported BF_3 • Modified SbF_3 • Supported liquid-acid catalysts	• Less corrosive • Safe handling • Fewer environmental problems
Isomerization	Conversion of C5/C6 alkanes into high-octane branched isomers	• Pt/Al_2O_3 • $Pt/SiO2\text{-}Al_2O_3$ • Modernite (zeolite)	• Solid super acid catalysts (e.g., sulfonated zirconia)	• Low temperatures • Increased conversion • Less cracking
Diesel Production				
Middle distillate hydrotreating	Diesel desulfurization	• $Co\text{-}Mo/Al_2O_3$	• High metal $Co\text{-}Mo/Al_2O_3$ with modified support pore structure	• Sulfur removal to < 500 ppm.
Middle distillate aromatics hydrdogenation	Production of low aromatics diesel	• $Ni\text{-}Mo/Al_2O_3$	• $Ni\text{-}Mo/Al_2O_3$ • Noble metal-zeolite combination in two-stage process	• Aromatics hydrogenation to acceptable low aromatics levels in diesel
VGO hydrotreating	FCC feed pretreatment to reduce sulfur and nitrogen levels	• $Co\text{-}Mo/Al_2O_3$	• $Co\text{-}Mo/Al_2O_3$ with improved formulation & pore structure • Ni-Mo/Zeolite + amorphous $SiO_2\text{-}Al_2O_3$	• Increased activity for N & S removal • Improved cycle length • Increased throughput • Mild hydrocracking • Increased middle distillate selectivity
Gas oil hydrocracking	Conversion of heavy gas oils to lighter products (gasoline & diesel)	• $Ni\text{-}Mo/Al_2O_3$ • $Ni\text{-}W/Al_2O_3$	• Ni-W/modified Al_2O_3 • $Ni\text{-}W/SiO_2\text{-}Al_2O_3$ • Ni-W/Zeolite + amorphous $SiO_2\text{-}Al_2O_3$	• Increased middle distillate selectivity • superior quality middle distillates • Increased catalyst life

FCC: Fluidized Catalytic Cracker
GSR: Gasoline Sulfur reduction
RE: Rare Earth
US: Ultra Stable
VGO: Vacuum gas oil
Y & ZSM-5: Crystalline forms y zeolite catalyst

Reaction Type and Reactor Choice

- Reaction mechanism (order, series of parallel reaction pathways, reversible or not) influences pollution prevention and strategies
- Mechanism details determine optimum temp, RTD and mixing
- Reactor operation influences conversion, selectivity, yield, by-product and waste formation
- For pollution prevention, very high yield, high selectivity for desired product and low selectivity for byproducts.

- Typical **reactor efficiency** measure for reaction yield (ratio of exiting product concentration to inlet reactant, ($[P] / [R]_0$); range from 0~1
- **Modified selectivity** as the ratio of exiting product concentration to the sum of product and byproduct (waste), ($[P] / ([P]+[W]) = [P] / [$ Reactant consumed $]$; range from 0~1

Parallel Reaction

$A \xrightarrow{k_D} D$ (*Desired Product*)

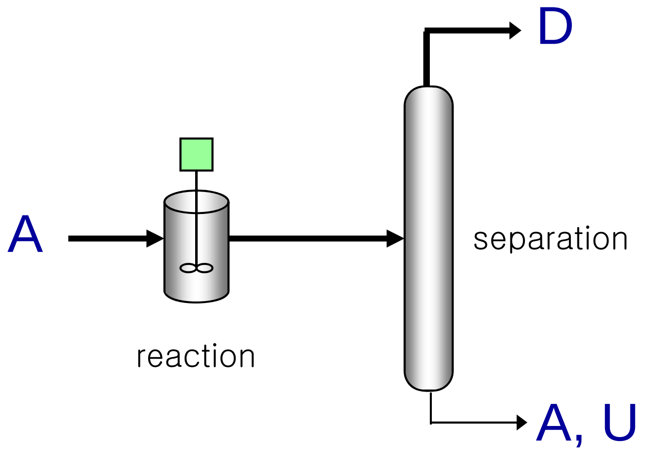
$A \xrightarrow{k_U} U$ (*Undesired Product*)

Competing or side rxn

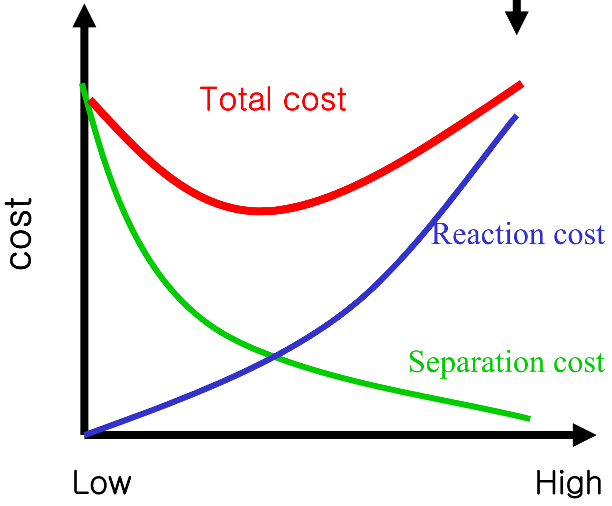
The economic incentive

Maximize the formation of D

Minimize the formation of U



Rxn-separation system producing both D & U



Efficiency of a reactor system

Rate selectivity parameter, S

$$A \xrightarrow{k_D} D \text{ (\textit{Desired Product})} \qquad r_D = k_D C_A^{\alpha_1}$$

$$A \xrightarrow{k_U} U \text{ (\textit{Undesired Product})} \qquad r_U = k_U C_A^{\alpha_2}$$

The rate laws are

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

$$r_D = k_D C_A^{\alpha_1}$$

$$r_U = k_U C_A^{\alpha_2}$$

Selectivity tells us how one product is favored over another when we have multiple reactions.

$$\boxed{S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}} = \frac{\textbf{Rate of formation of D}}{\textbf{Rate of formation of U}}$$

Rate selectivity parameter = Instantaneous selectivity

Maximizing S_{DU} for one reactant

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

- **Case 1: $\alpha_1 > \alpha_2$, $a = \alpha_1 - \alpha_2$**

$$\boxed{S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{a}}$$

maximize S_{DU}

- keeping the concentration of reactant A as high as possible during the rxn

- in gas phase rxn, we should run it without inerts and at high pressures to keep C_A high

- in liquid phase rxn, the use of diluents should be keep to a minimum

- use a batch or plug-flow reactor

Maximizing S_{DU} for one reactant

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

- **Case 2: $\alpha_2 > \alpha_1$, a = $\alpha_2 - \alpha_1$**

$$\boxed{S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} \frac{1}{C_A^a}}$$

maximize S_{DU}

- keeping the concentration of reactant A as low as possible during the rxn

- in gas phase rxn, we should run it with inerts and at low pressures to keep C_A low

- in liquid phase rxn, the use of diluents should be keep to a maximum

- use a CSTR or recycle reactor (product stream act as a diluent)

Maximizing S_{DU} for one reactant

Whether the reaction should be run at high or low T

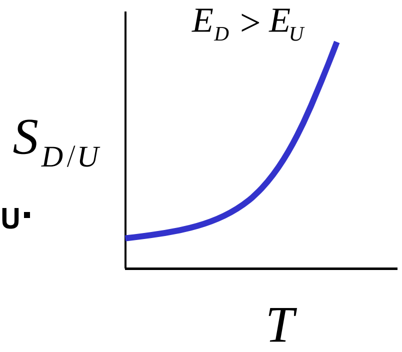
$$\boxed{\frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-\frac{E_D - E_U}{RT}}}$$

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}$$

- **Case 3: $E_D > E_U$ → high T**

- k_D (r_D) increases more rapidly increasing temperature than does the k_U.

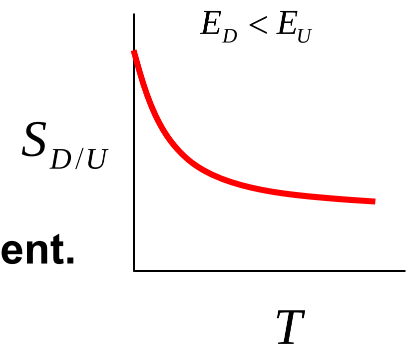
- keeping the temperature as high as possible to maximize S_{DU}.



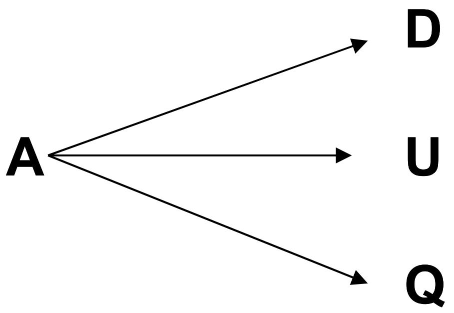
- **Case 4: $E_D < E_U$ → low T**

- keeping the temperature as low as possible to maximize S_{DU}

- not so low that the desired rxn does not proceed to any significant extent.



Ex 6-1 Minimizing unwanted products (U & Q) for a single reactant



$$r_D = 0.0002\, e^{36{,}000\left(\frac{1}{300}-\frac{1}{T}\right)} C_A \qquad (1)$$

$$r_U = 0.0018\, e^{25{,}000\left(\frac{1}{300}-\frac{1}{T}\right)} C_A^{1.5} \qquad (2)$$

$$r_Q = 0.00452\, e^{5{,}000\left(\frac{1}{300}-\frac{1}{T}\right)} C_A^{0.5} \qquad (3)$$

- Pre-exponential factors are comparable
- the activation energies of (1) & (2) are much greater than that of (3).
- at high temperature $r_Q << r_D, r_U$

$$\boxed{S_{D/(X+Y)} = \frac{r_D}{r_X + r_Y}}$$

$$S_{DQ} = \frac{r_D}{r_Q} \cong \text{very large} \qquad (4)$$

$$S_{DU} = \frac{r_D}{r_U} = \frac{0.11\, e^{11{,}000\left(\frac{1}{300}-\frac{1}{T}\right)}}{C_A^{0.5}} \qquad (5)$$

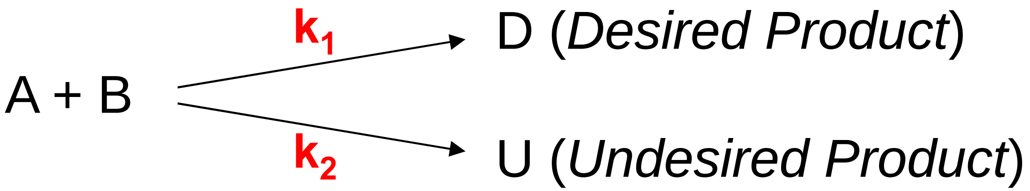
- From (5), S_{DU} minimized at low concentration of A

1. High Temperatures (to minimize the formation of Q)

2. Low concentration of A (to minimize the formation of U)

- Adding inerts, using low pressures, using CSTR or recycled reactor

Maximizing S_{DU} for two reactants



$$A + B \xrightarrow{k_1} D \text{ (Desired Product)}$$

$$A + B \xrightarrow{k_2} U \text{ (Undesired Product)}$$

The rate laws are

$$-r_A = k_1 C_A^{\alpha_1} C_B^{\beta_1} + k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

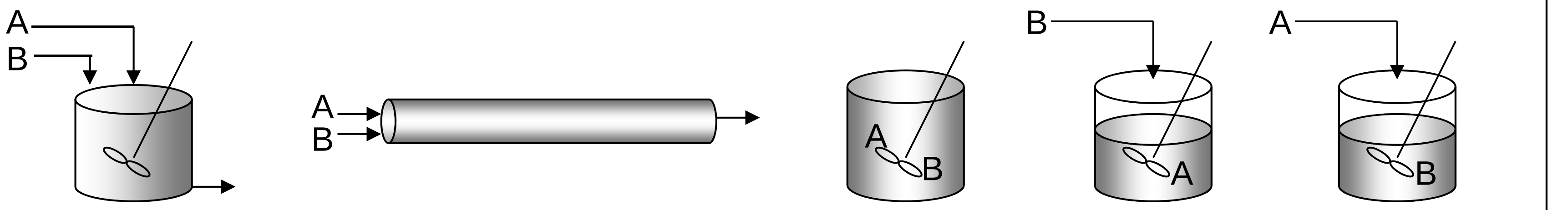
$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

$$\boxed{S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}}$$

Rate selectivity parameter=Instantaneous selectivity

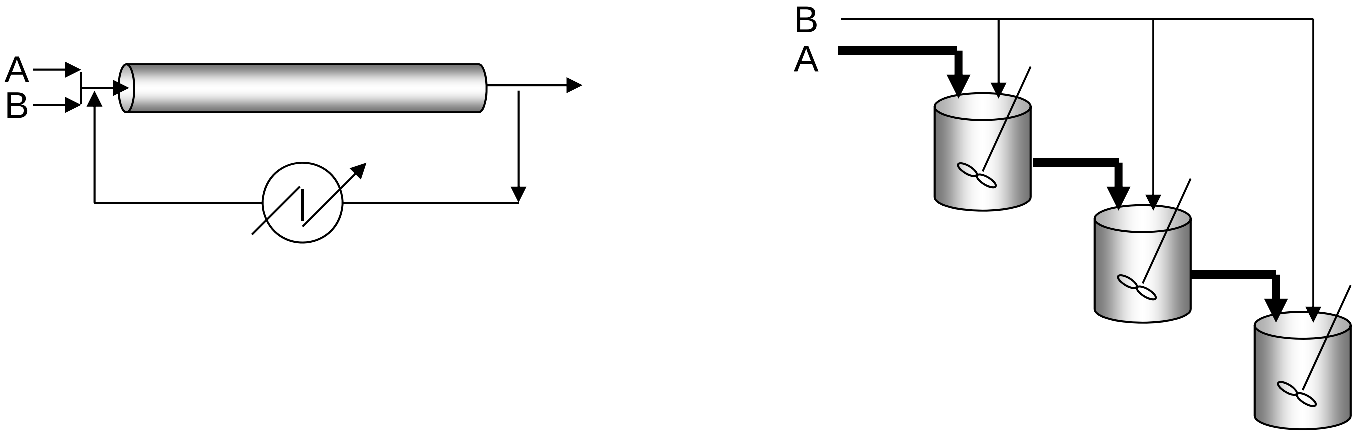
Figure 6-3

Different reactors and schemes for minimizing the unwanted product



(a) CSTR (b) tubular reactor (c) batch (d) semibatch 1 (e) semibatch 2

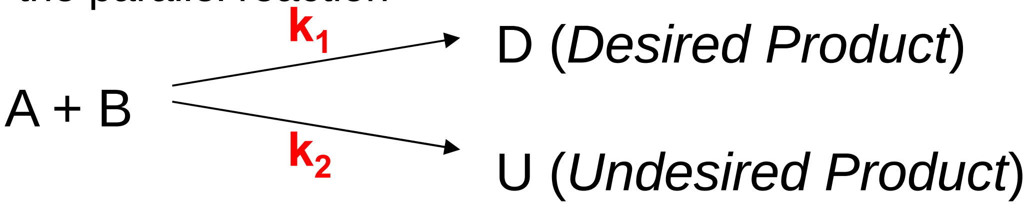
(f) Tubular reactor with side streams (g) Tubular reactor with side streams



(h) Tubular reactor with recycle (i) Series of small CSTRs

Ex. 6-2 Minimizing unwanted products for two reactants

for the parallel reaction



A + B

k_1

D (*Desired Product*)

k_2

U (*Undesired Product*)

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$
$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Case I : $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$, $a = \alpha_1 - \alpha_2 > 0$, $b = \beta_1 - \beta_2 > 0$

the rate selectivity parameter

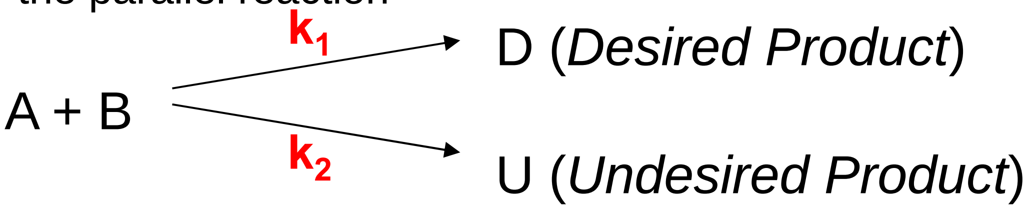
$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^a C_B^b$$

To maximize the S_{DU}, maintain the concentration of both A and B as high as possible

- a tubular reactor
- a batch reactor
- high pressures (if gas phase)

Ex. 6-2 Minimizing unwanted products for two reactants

for the parallel reaction



A + B $\xrightarrow{k_1}$ D (*Desired Product*)

A + B $\xrightarrow{k_2}$ U (*Undesired Product*)

$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$
$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Case II : $\alpha_1 > \alpha_2$, $\beta_1 < \beta_2$, $a = \alpha_1 - \alpha_2 > 0$, $b = \beta_2 - \beta_1 > 0$

the rate selectivity parameter

$$S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_A^a}{k_2 C_B^b}$$

To maximize the S_{DU}, maintain C_A high and C_B low.

- a semibatch reactor in which B is fed slowly into A. (Fig. 6-3d)
- a tubular reactor with side stream of B continually (Fig. 6-3f)
- a series of small CSTRs with A fed only to the first reactor (Fig. 6-3i)

Ex. 6-2 Minimizing unwanted products for two reactants

for the parallel reaction

$$A + B \xrightarrow{k_1} D \text{ (\textit{Desired Product})}$$

$$A + B \xrightarrow{k_2} U \text{ (\textit{Undesired Product})}$$

$$\boxed{\begin{aligned} r_D &= k_1 C_A^{\alpha_1} C_B^{\beta_1} \\ r_U &= k_2 C_A^{\alpha_2} C_B^{\beta_2} \end{aligned}}$$

Case III : $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$, $a = \alpha_2 - \alpha_1 > 0$, $b = \beta_2 - \beta_1 > 0$

the rate selectivity parameter

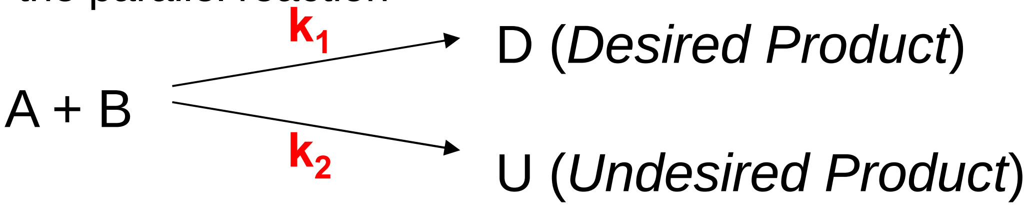
$$\boxed{S_{DU} = \frac{r_D}{r_U} = \frac{k_1}{k_2 C_A^a C_B^b}}$$

To maximize the S_{DU}, maintain the concentration of both A and B as low as possible

- a CSTR
- a tubular reactor in which there is a large recycle ratio
- a feed diluted with inerts
- low pressures (if gas phase)

Ex. 6-2 Minimizing unwanted products for two reactants

for the parallel reaction



$$\boxed{\begin{aligned} r_D &= k_1 C_A^{\alpha_1} C_B^{\beta_1} \\ r_U &= k_2 C_A^{\alpha_2} C_B^{\beta_2} \end{aligned}}$$

Case IV : $\alpha_1 < \alpha_2$, $\beta_1 > \beta_2$, $a = \alpha_2 - \alpha_1 > 0$, $b = \beta_1 - \beta_2 > 0$

the rate selectivity parameter

$$\boxed{S_{DU} = \frac{r_D}{r_U} = \frac{k_1 C_B^b}{k_2 C_A^a}}$$

To maximize the S_{DU}, maintain the concentration of both A and B as high as possible

- a semibatch reactor in which A is slowly fed to B (Fig. 6-3e)
- a tubular reactor with side stream of A (Fig. 6-3g)
- a series of small CSTRs with B fed only to the first reactor (reverse of Fig. 6-3i)

Maximizing the desired product in series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- In parallel rxns, maximize the desired product
  - adjusting the reaction conditions
  - choosing the proper reactor

- In series rxns, maximize the desired product
  - adjusting the space-time for a flow reactor
  - choosing real-time for a batch reactor

Maximizing the desired product in series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

- If the first reaction is slow and second reaction is fast, it will be extremely difficult to produce species B.

- If the first reaction (formation of B) is fast and the reaction to form C is slow, a large yield of B can be achieved.

- However, if the reaction is allowed to proceed for a long time in a batch reactor or if the tubular flow reactor is too long, the desired product B will be converted to C.

Ex. 6-3 Maximizing the yield of the intermediate product

The oxidation of ethanol to form acetaldehyde is carried out on a catalyst of 4 wt% Cu-2wt% Cr on Al_2O_3. Unfortunately, acetaldehyde is also oxidized on this catalyst to form carbon dioxide. The reaction is carried out in a dilute concentrations (ca. 0.1% ethanol, 1% O_2, and 98.9% N_2). Consequently, the volume change with the reaction can be neglected. Determine the concentration of acetaldehyde as a function of space time.

$$\mathrm{CH_3CH_2OH(g)} \xrightarrow[+\frac{1}{2}O_2 - H_2O]{k_1} \mathrm{CH_3CHO} \xrightarrow[+\frac{5}{2}O_2 - 2H_2O]{k_2} \mathrm{2CO_2}$$

The rxns are irreversible and first-order in ethanol and acetaldehyde, respectively.

Solution

Because O_2 is in excess, we can write the preceding series reaction as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The preceding series reaction can be written as

$$\text{Reaction (1)}\ A \xrightarrow{k_1} B$$

$$\text{Reaction (2)}\ B \xrightarrow{k_2} C$$

1. **Mole balance on A:**

$$\frac{dF_A}{dW} = r'_A \tag{E6-4.1}$$

a. **Rate law:**

$$-r'_A = k_1 C_A$$

b. **Stoichiometry** (Dilute concentrations: $y_{A0} = 0.001$) $\therefore\ v = v_0$

$$F_A = C_A v_0$$

c. **Combining**, we have

$$v_0 \frac{dC_A}{dW} = -k_1 C_A \tag{E6-4.2}$$

Let $\tau' = W/v_0 = \rho_b V/v_0 = \rho_b \tau$, where ρ_b is the bulk density of the catalyst.

d. Integrating with $C_A = C_{A0}$ at $W = 0$ gives us

$$\boxed{C_A = C_{A0} e^{-k_1 \tau'}} \tag{E6-4.3}$$

2. **Mole balance on B:**

$$\frac{dF_B}{dW} = r'_{B_{net}} \tag{E6-4.4}$$

a. **Rate law** (net):

$$r'_{B_{net}} = r'_{B_{rxn1}} + r'_{B_{rxn2}}$$
$$r'_{B_{net}} = k_1 C_A - k_2 C_B \tag{E6-4.5}$$

b. **Stoichiometry:**

$$F_B = v_0 C_B$$

c. **Combining** yields

$$v_0 \frac{dC_B}{dW} = k_1 C_A - k_2 C_B \tag{E6-4.6}$$

Substituting for C_A, dividing v_0 into W and rearranging, we have

$$\frac{dC_B}{d\tau'} + k_2 C_B = k_1 C_{A0} e^{-k_1 \tau'}$$

d. **Using** the integrating factor gives us

$$\frac{d(C_B e^{+k_2 \tau'})}{d\tau'} = k_1 C_{A0}\, e^{(k_2 - k_1)\tau'}$$

At the entrance to the reactor, $W = 0$, $\tau' = W/v_0 = 0$, and $C_B = 0$. Integrating, we get

$$\boxed{C_B = k_1 C_{A0} \left(\frac{e^{-k_1 \tau'} - e^{-k_2 \tau'}}{k_2 - k_1} \right)} \qquad \text{(E6-4.7)}$$

The concentrations of A, B, and C are shown in Figure E6-4.1.

3. **Optimum yield.** The concentration of B goes through a maximum at a point along the reactor. Consequently, to find the optimum reactor length, we need to differentiate Equation (E6-4.7):

$$\frac{dC_B}{d\tau'} = 0 = \frac{k_1 C_{A0}}{k_2 - k_1} \left(-k_1 e^{-k_1 \tau'} + k_2 e^{-k_2 \tau'}\right) \qquad \text{(E6-4.8)}$$

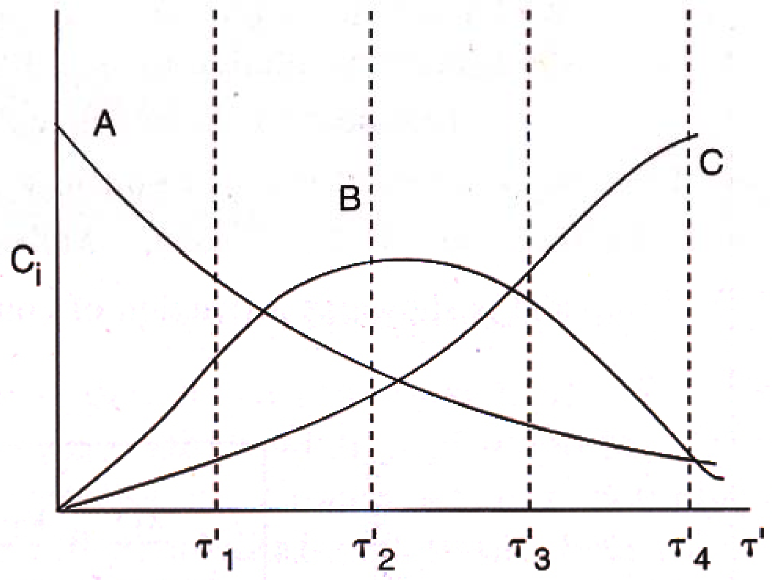


Figure E6-4.1 Concentration profiles down a PBR in terms of space time $\tau' = W/v_0$. [*Note:* $\tau' = \rho_b(W/\rho_b)/v_0 = \rho_b(V/v_0) = \rho_b\tau$.]

Solving for τ'_{opt} gives

$$\boxed{\begin{aligned} \tau'_{opt} &= \frac{1}{k_1-k_2}\ln\frac{k_1}{k_2} && \text{(E6-4.9)} \\ W_{opt} &= \frac{v_0}{k_1-k_2}\ln\frac{k_1}{k_2} && \text{(E6-4.10)} \end{aligned}}$$

The corresponding conversion of A at the maximum C_B is

$$X_{opt} = \frac{C_{A0}-C_A}{C_{A0}} = 1-e^{-k_1\tau'_{opt}}$$

Using Equation (E6-4.9) to substitute for τ'_{opt}

$$\boxed{X_{\text{opt}} = 1-\exp\left[-\ln\left(\frac{k_1}{k_2}\right)^{k_1/(k_1-k_2)}\right] = 1-\left(\frac{k_1}{k_2}\right)^{k_1/(k_2-k_1)}} \tag{E6-4.11}$$

4. Mole Balance on *C*:

$$\frac{dC_{\text{C}}}{d\tau'} = r'_{\text{C}} = k_2 C_{\text{B}} = \frac{k_1 k_2 C_{\text{A0}}}{k_2-k_1}[e^{-k_1\tau'} - e^{-k_2\tau'}] \tag{E6.4-12}$$

At the entrance to the reactor, no C is present, so the boundary condition is

$$\tau' = 0 \quad C_{\text{C}} = 0$$

$$\boxed{C_{\text{C}} = \frac{C_{\text{A0}}}{k_2-k_1}[k_2[1-e^{-k_1\tau'}]-k_1[1-e^{-k_2\tau'}]]} \tag{E6.4-13}$$

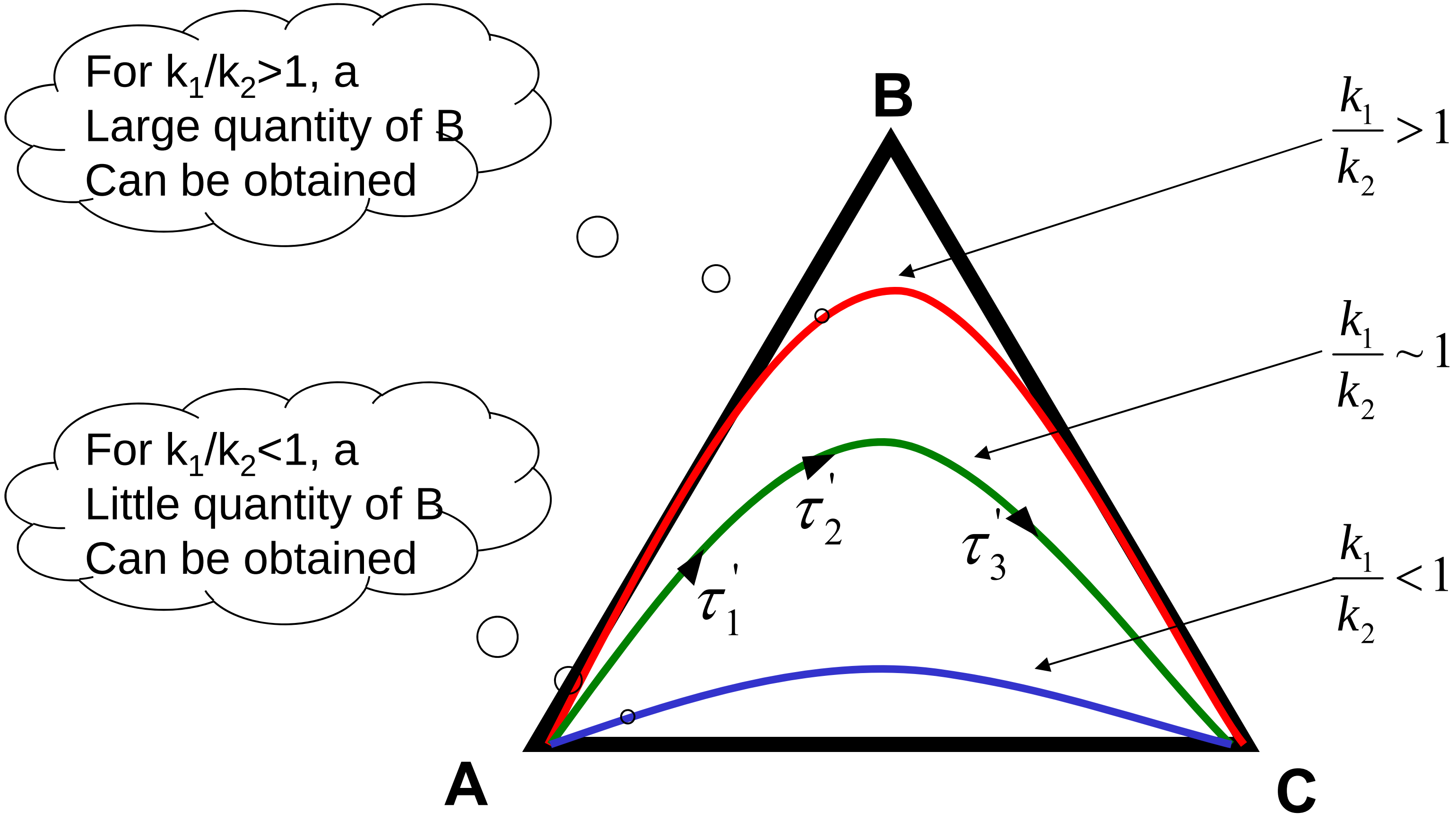
Note as $t \rightarrow \infty$ then $C_{\text{C}} = C_{\text{A0}}$ as expected

We note that the concentration of C, C_{C}, could have also been obtained from the overall mole balance

$$\boxed{C_{\text{C}} = C_{\text{A0}} - C_{\text{A}} - C_{\text{B}}} \tag{E6.4-14}$$

Reaction paths for different ks in series reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$



For $k_1/k_2>1$, a Large quantity of B Can be obtained

For $k_1/k_2<1$, a Little quantity of B Can be obtained

1st rxn is slow
2nd rxn is fast

Long rxn time in batch or long tubular reactor
-> B will be converted to C

Examples :

1. Parallel reaction pathway

(partial oxidation of ethylene to ethylene oxide, whereas parallel reaction converts ethylene to by-products, CO_2 and water)

Pollution generation with irreversible 1st order parallel reaction

$$\boldsymbol{R} \xrightarrow{k_p} \boldsymbol{P}$$

$$\boldsymbol{R} \xrightarrow{k_w} \boldsymbol{W}$$

where R is reactant, P is product and W, the waste byproduct
k_p and k_w are the 1st order reaction rate constant

Parallel reaction pathway

$$R \xrightarrow{k_p} P$$

$$R \xrightarrow{k_w} W$$

Relative concentrations of P and W are affected by k_p / k_w (Fig. 9.3-1)

- To achieve max yields, RTD must be about 5 times the reaction time constants $(k_p + k_w)^{-1}$
- Reaction selectivity is constant and independent of RTD of 1st order irreversible isothermal parallel reactions.
- In reality, selectivity is dependent on the RTD and this parameter is the factor for pollution prevention

$$\boldsymbol{R} \xrightarrow{k_p} \boldsymbol{P}$$

$$\boldsymbol{R} \xrightarrow{k_w} \boldsymbol{W}$$

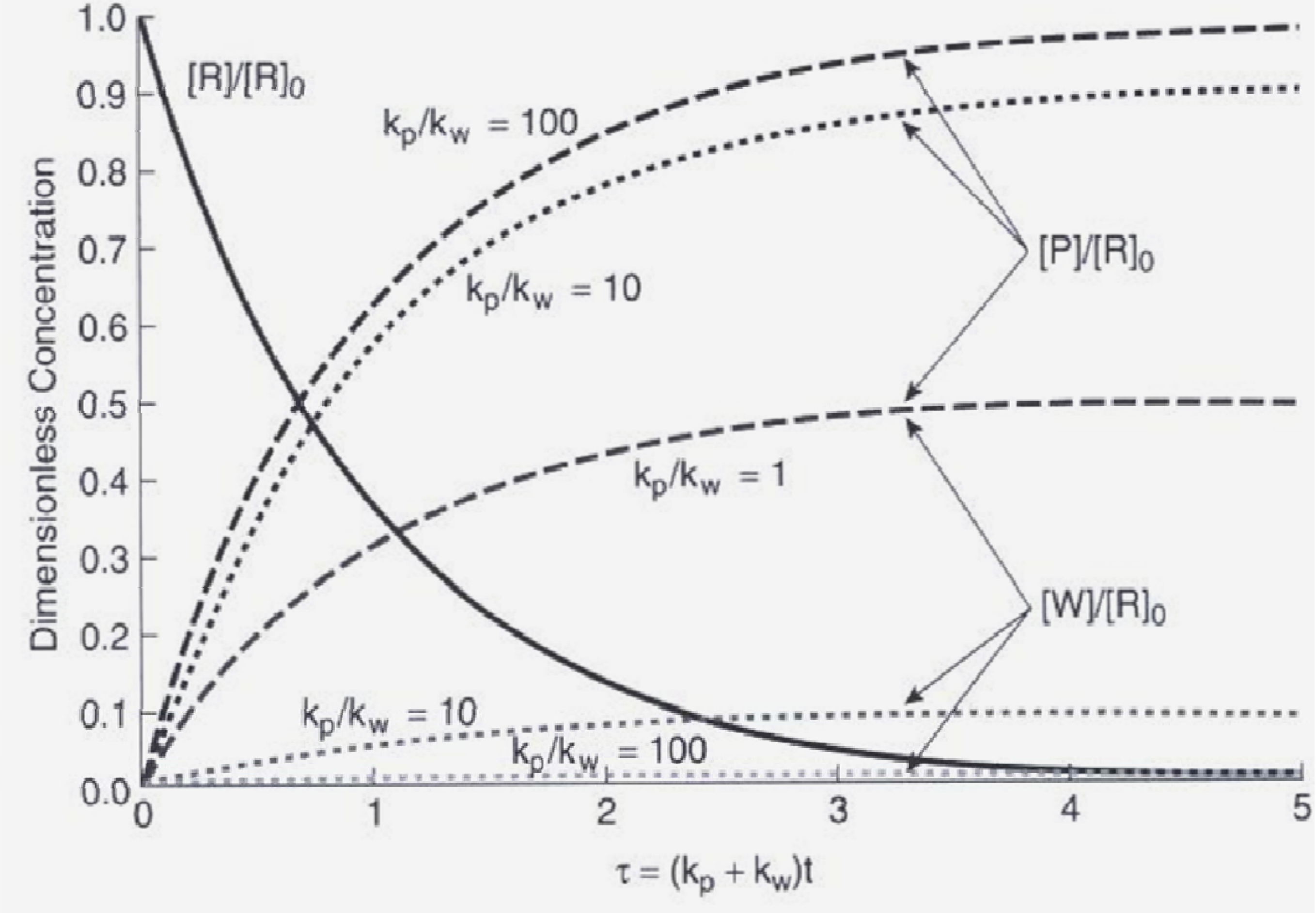


Fig. 9.3-1
Effect of ratio of k_p/k_w on the reactor outlet concentrations of products, reactants, and byproducts for a simple irreversible 1st order parallel reaction mechanism

Series reaction pathway

$$R \xrightarrow{k_p} P \xrightarrow{k_w} W$$

Rate of waste generation depends on the rate of production formation (Fig. 9.3-2)

- Longer RTD leads to not only more product formation but also more byproduct generation
- Amount of waste generation depends on the ratio of k_p / k_w and RTD
- For each ratio, k_p / k_w there is an optimum RTD that maximize the product concentration

$$R \xrightarrow{k_p} P \xrightarrow{k_w} W$$

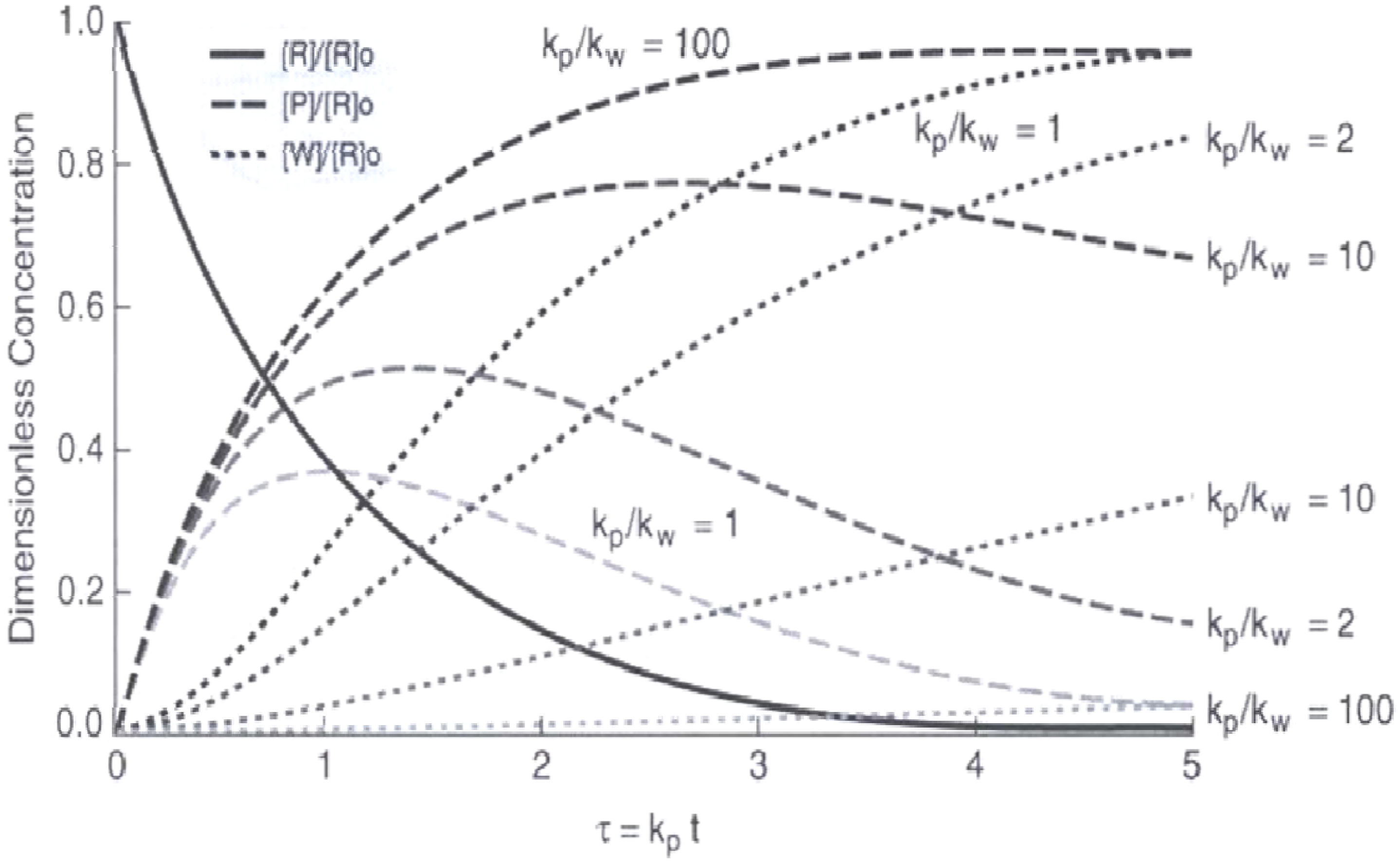


Fig. 9.3-2
Effect of product and waste reaction rate constants on product and waste concentrations in a 1st irreversible series reaction. The RTD has been made dimensionless using the product reaction rate constant

Series reaction pathway

Product yield and modified selectivity continues to decrease with time (Fig. 9.3-3) in series reaction

- At longer RTD, the rate of waste generation is greater than the rate of production formation

- To minimize waste generation in series reaction, operate reactor so that the ratio k_p/k_w is as large as possible and to control the RTD

- By removing product as it is being formed and before its concentration builds up in the reactor, then the byproduct can be minimized

$$\boldsymbol{R} \xrightarrow{k_p} \boldsymbol{P} \xrightarrow{k_w} \boldsymbol{W}$$

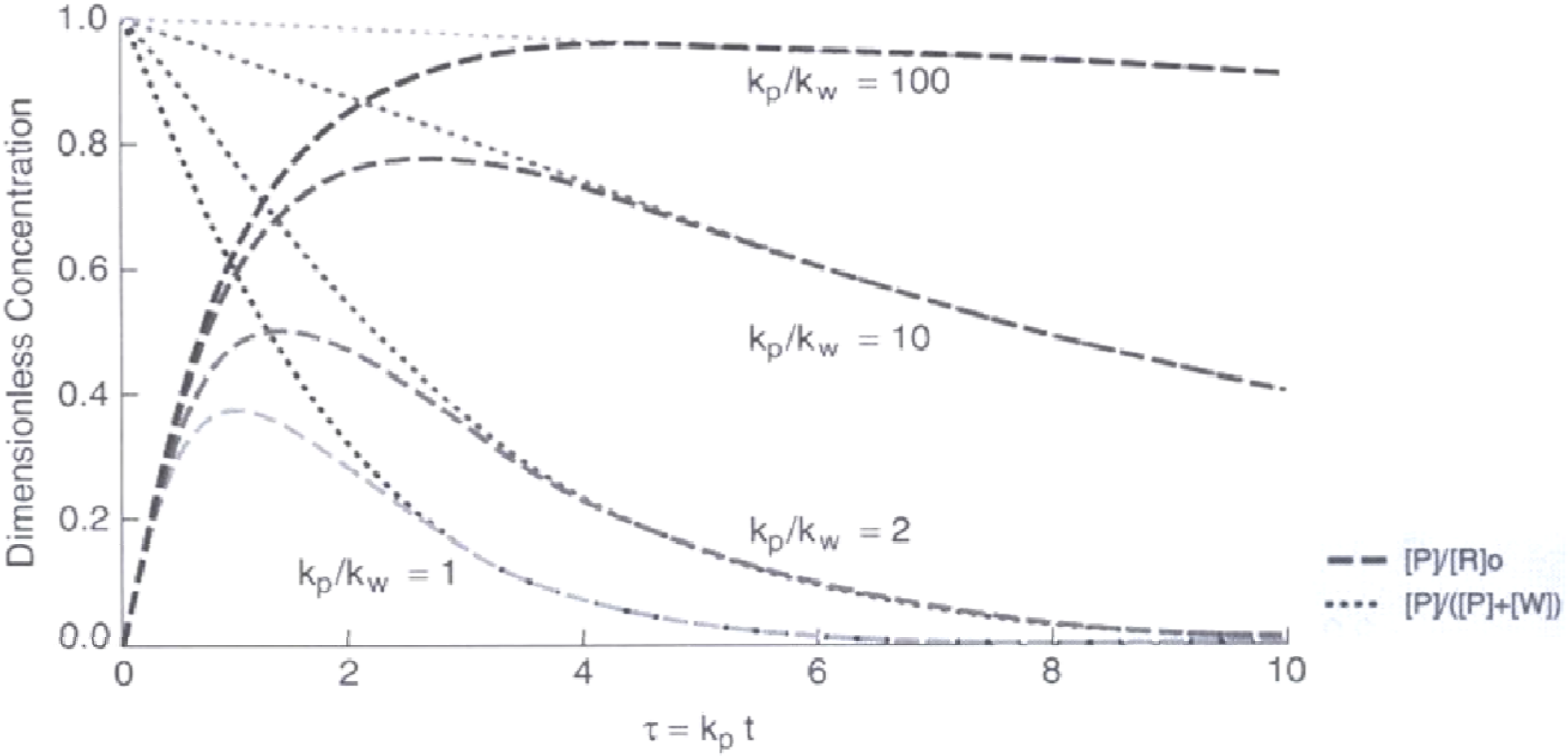


Fig. 9.3-3
Effect of product and waste reaction rate constants on product yield and modified selectivity for 1st order irreversible series reaction.

Reversible Reaction pathway

- Another important category of reactions **(Fig. 9.3-4)** in parallel and series modes
- Reversible reactions inhibit full conversion of reactants
- RTD is a key operating parameter
- Selectivity improvement for reversible reaction, operated at equilibrium, can be achieved by utilizing the concept of recycle to extinction.**(Example)** steam reforming of methane

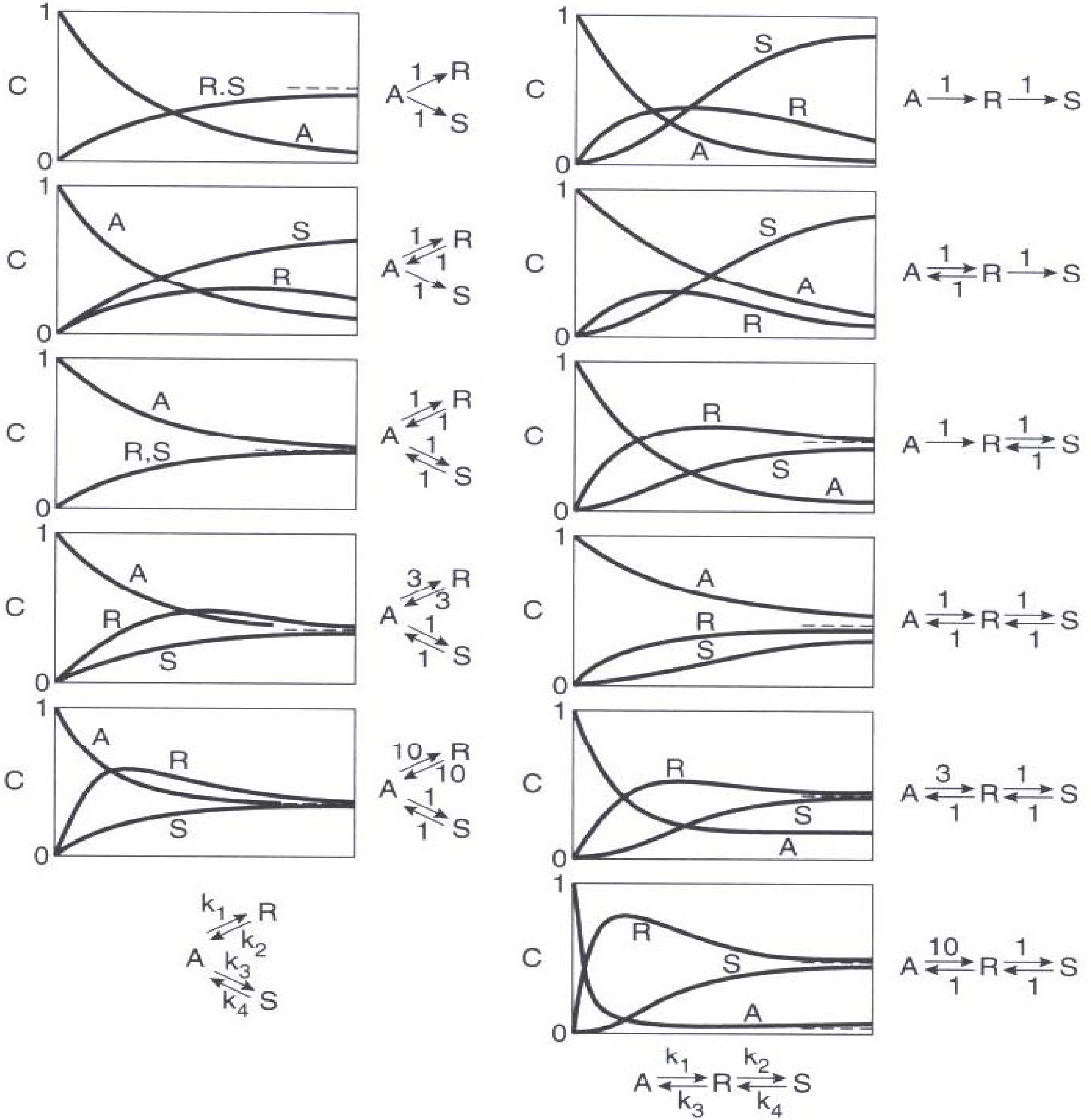


Fig. 9.3-4

Product and byproduct profiles for reversible parallel and series reactions

Reversible Reaction pathway

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Both reactions are reversible at equilibrium

- When CO_2 is recovered and recycled back to the reactor, it decomposes in the reactor as fast as it forms

- No net conversion of CH_4 to CO_2 occurs

- This requires additional operating costs, but there is no selectivity loss of reactant, the process is cleaner

- It may be lowest cost option overall

Reactor combined with a separator that recycles reactants and byproducts (Fig. 9.3-5)

- Can be operated such that all reactants fed to the reactor are converted to product with no net waste generation
- Selectivity improvements can be by separative reactors

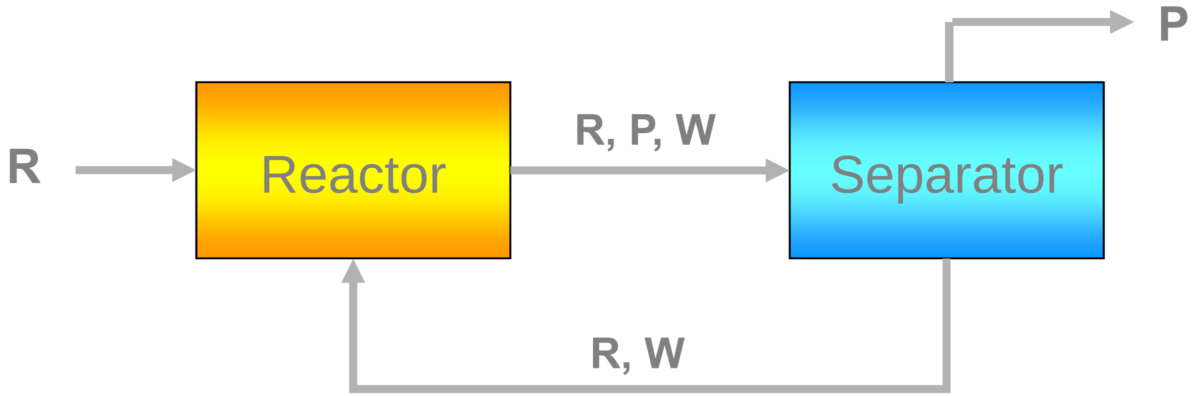


Fig. 9.3-5
Process flow diagram illustrating the concept of recycling to extinction for reversible reactions

Reactor Operation

Reaction Temperature

- Reaction Temp. influence the conversion, yield and selectivity
- For irreversible 1st order parallel reaction, the selectivity indicator is

$$\frac{k_p[R]}{k_w[R]} = \frac{k_p}{k_w} = \frac{A_p e^{-(E_p/RT)}}{A_w e^{-(E_w/RT)}}$$

where A the frequency factor and
E the activation energy

$$\Delta\frac{k_p}{k_w} = \frac{e^{-(E_p/RT_1)}/e^{-(E_w/RT_1)}}{e^{-(E_p/RT_0)}/e^{-(E_w/RT_0)}} = \frac{e^{-(E_p-E_w)/RT_1}}{e^{-(E_p-E_w)/RT_0}}$$

Reactor Operation

Reaction Temperature

Calculate change of the k_p/k_w ratio as the function of T change to a new T_1 w.r.t. given T_0 **(Fig. 9.3-6)**

- when $E_p > E_w$ the ratio increases with with increasing T and decreases with decreasing T
- Thus, pollution can be prevented in parallel rxn by increasing reactor T when $E_p > E_w$
- The opposite holds true when $E_p < E_w$
- When the difference E_p and E_w increases, T has more influence

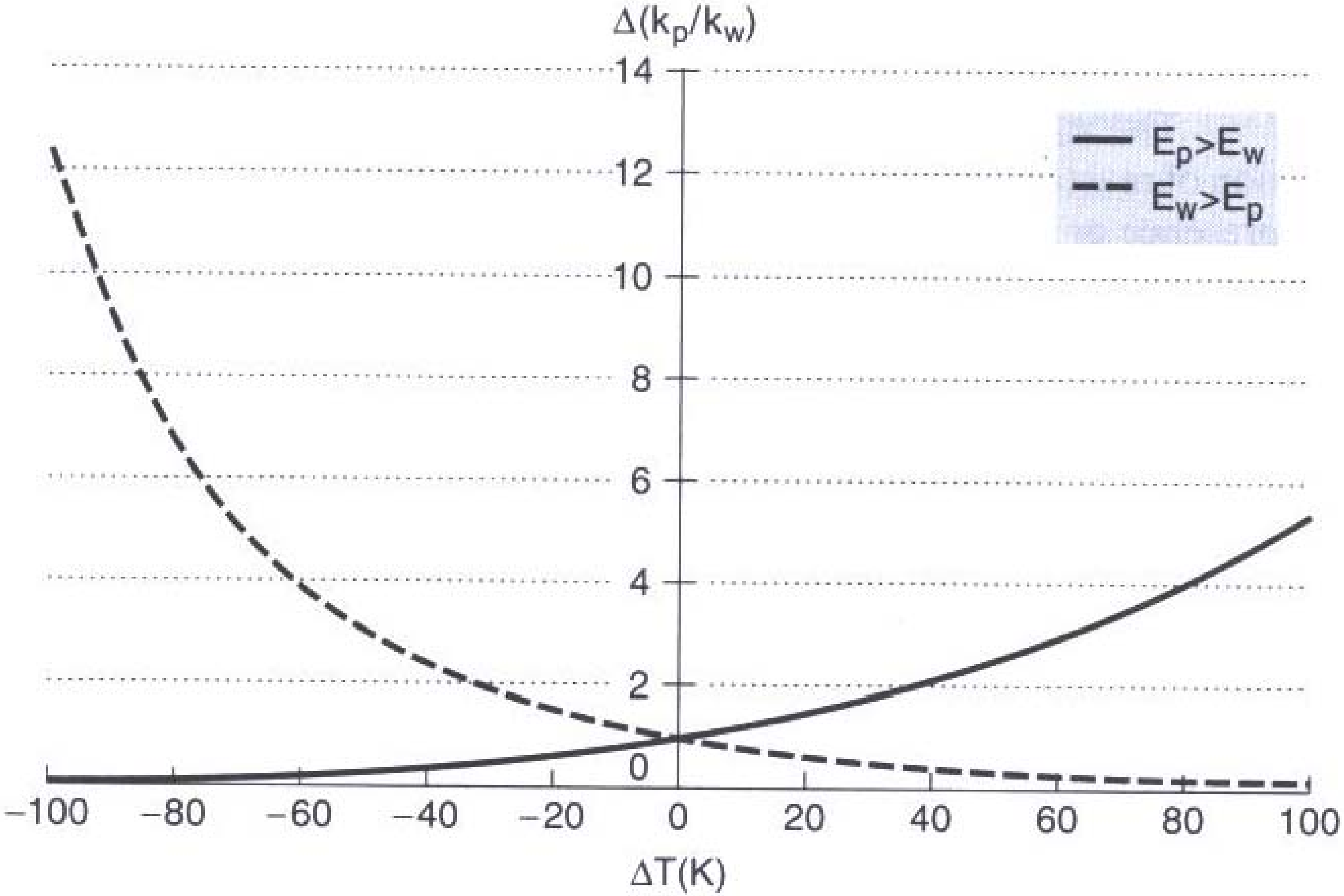


Fig. 9.3-6

Effect of T on the ratio of rate constants for 1st order parallel and irreversible reaction

Reactor Operation

Mixing

(Complex multiple reactions can be influenced by the intensity of mixing in CSTR)

- For irreversible reaction, the yield and selectivity may be altered compared to the case where the reactants are mixed instantaneously to a molecular level *(may be generate waste byproduct a lot)*

- Rate can be reduced due to diffusional limitations between segregated elements of the reacting mixture

- Imperfect mixing is particularly evident for rapidly reacting systems

Competitive consecutive reaction in CSTR (series parallel reaction)

$$\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned}$$

 # kinetics of nitration and halogenation of hydrocarbons, saponification of polyesters

- A is initially charged and B is added continuously as a solution
- R is the desired product and S is byproduct
- If rxn is 1st order, mixing will not affect selectivity
- If it is 2nd order, the presence of local excess C can cause overreaction of R to S This mixing effect occurs for both homo- and heterogeneous reaction systems for batch or semi-batch reactor

Ex. Iodization of L-tyrosine in aqueous solution (Fig. 9.3-7)

- *study of effects of T, initial conc. of A (A_0), rate of addition of B, agitation rate of the vessel impeller, presence or absence of baffling in the reactor.*
- *correlation for all of these parameters was found between the ratio of measured yield to expected yield(Y / Y_{exp}) vs. dimensionless quantity, $(k_1 B_0 \tau) (A_0 / B_0)$,*

where k_1 : *product reaction rate constant (L/gmol.sec)*

k_2 : *by product reaction rate constant (L/gmol.sec)*

τ : *microtime scale for mixing of eddies of pure B with bulk liquid(sec)*

Y : *measure yield* (R/A_0)

$(k_1 B_0 \tau)$: *extent of conversion of A and B under conditions of partial segregation*

A/A_0 : *fraction of reactant A remaining at the end of the reaction*

Y_{exp} : *expected yiled (perfect mixing)* $= R/A_0$

- Correlation fitting the date is in **Fig. 9.3-8**
  - *measured* $Y/Y_{exp} = 0.66 \sim 0.98$ *depends on mixing intensity and other parameters*
  - *when,* $(k_1 B_0 \tau)(A_0/B_0) \leq 10^{-5}$, *then* $Y \approx Y_{exp}$, *this criterion allow us*
  - *mixing intensity for 2nd order competitive-consecutive rxn*
    $10^{-5} = (k_1 B_0 \tau)(A_0/B_0) = (k_1 \tau A_0)$
  - *rearranging and incorporating the Kolmogoroff theory*

$$\tau = \frac{10^{-5}}{A_0 k_1} = \frac{0.882 \nu^{3/4} L_f^{3/4}}{(u')^{7/4}}$$

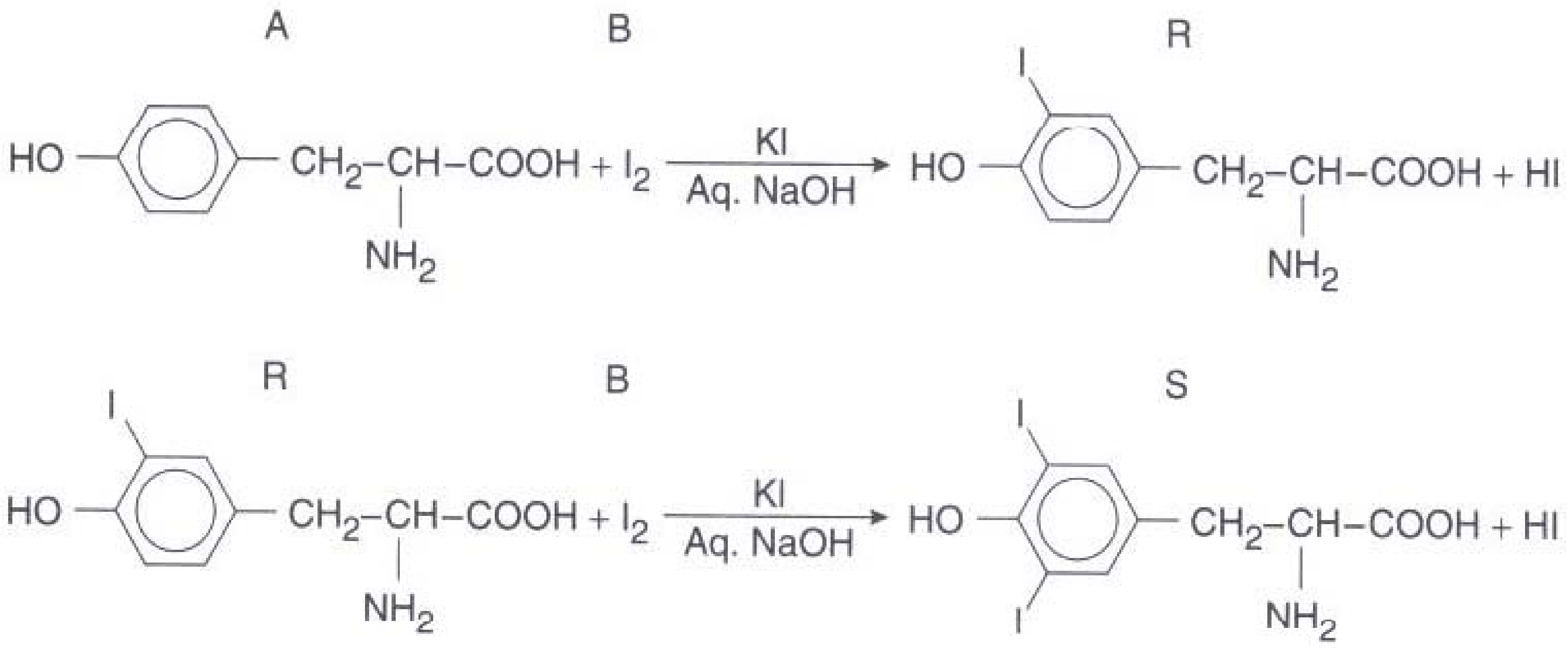


Fig. 9.3-7 *Iodization of L-tyrosine in aqueous solution*

- *correlation fitting the date is in* ***Fig. 9.3-8***

  - ***rearranging and incorporating the Kolmogoroff theory***

$$\tau = \frac{10^{-5}}{A_0 k_1} = \frac{0.882 \nu^{3/4} L_f^{3/4}}{(u')^{7/4}}$$

where L_f : *a characteristic length scale of the vessel (ft)*
u' : *fluctuating turbulent velocity, ft/sec*
ν : *kinematic viscosity,* ft^2 */sec*

  - ***Rearranging and incorporate a correlation for turbulent fluctuation velocity in a CSTR*** *for feed entering at the impeller (u"=0.45π DN)*

$$u' = \left[\frac{0.882 \nu^{3/4} L_f^{3/4}}{\left(\frac{10^{-5}}{A_0 k_1} \right)} \right]^{4/7} = 0.45 \pi DN$$

¶ *Thus, we can establish the impeller agitation speed(N) to ensure that mixing will not adversely affect the yield, given parameters*

Example 9.3-1, 9.3-2

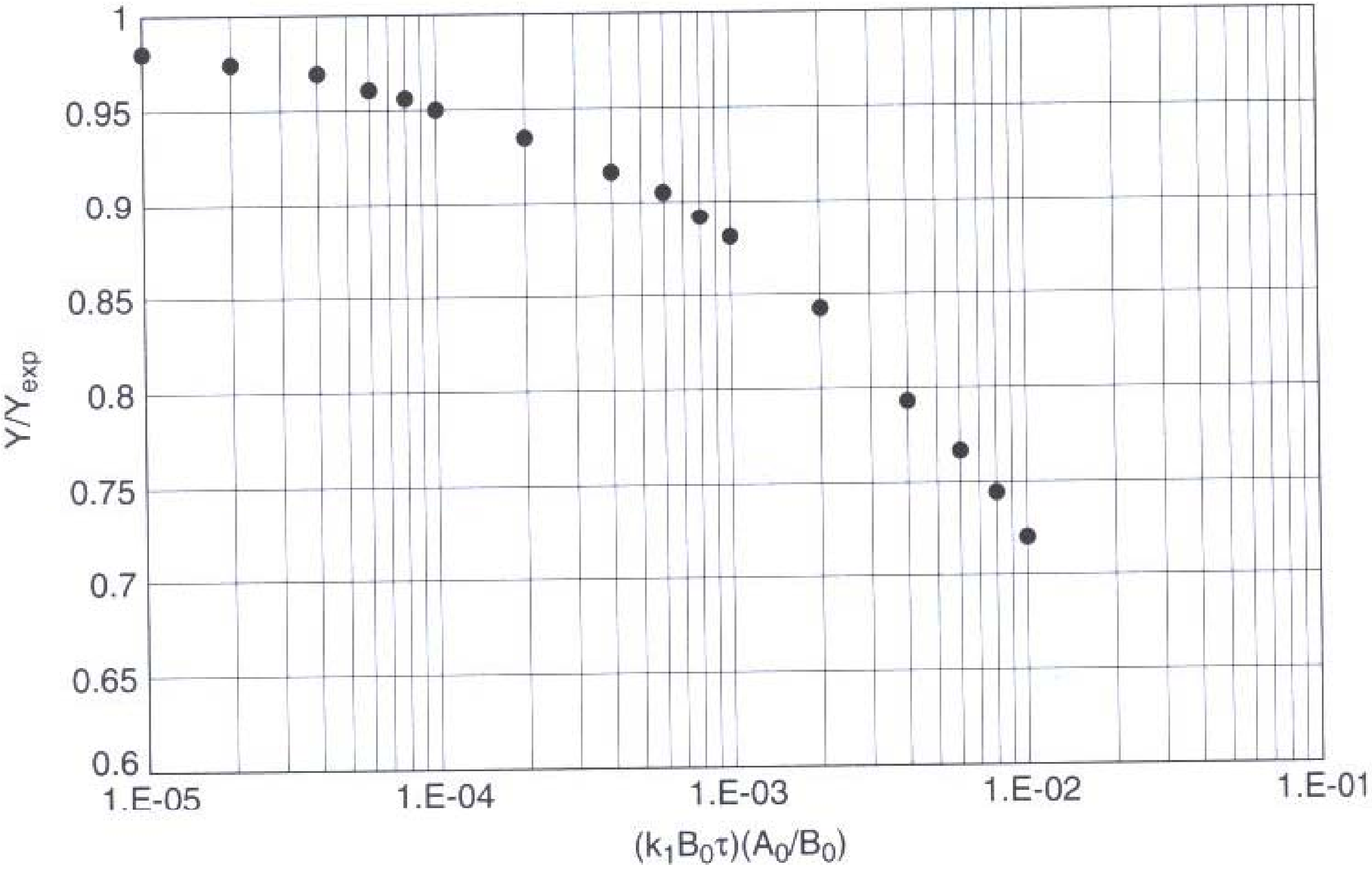


Fig. 9.3-8
Correlation of reaction yield efficiency with the mixing parameters for irreversible consecutive-competitive 2nd order reaction

Effect of Reactant Concentration

(selectivity is sensitive to initial concentration, since the rate of product and byproduct formation depends on concentration)

- For parallel irreversible reaction, the rates of formations are
  - *rate of product formation* = $k_p [R]^{np}$
  - *rate of waste generation* = $k_w [R]^{nw}$
- The ratio of these rates is an indicator of the selectivity toward product formation

$$\frac{k_p [R]^{n_p}}{k_w [R]^{n_w}} = \frac{k_p}{k_w} [R]^{-(n_p - n_w)}$$

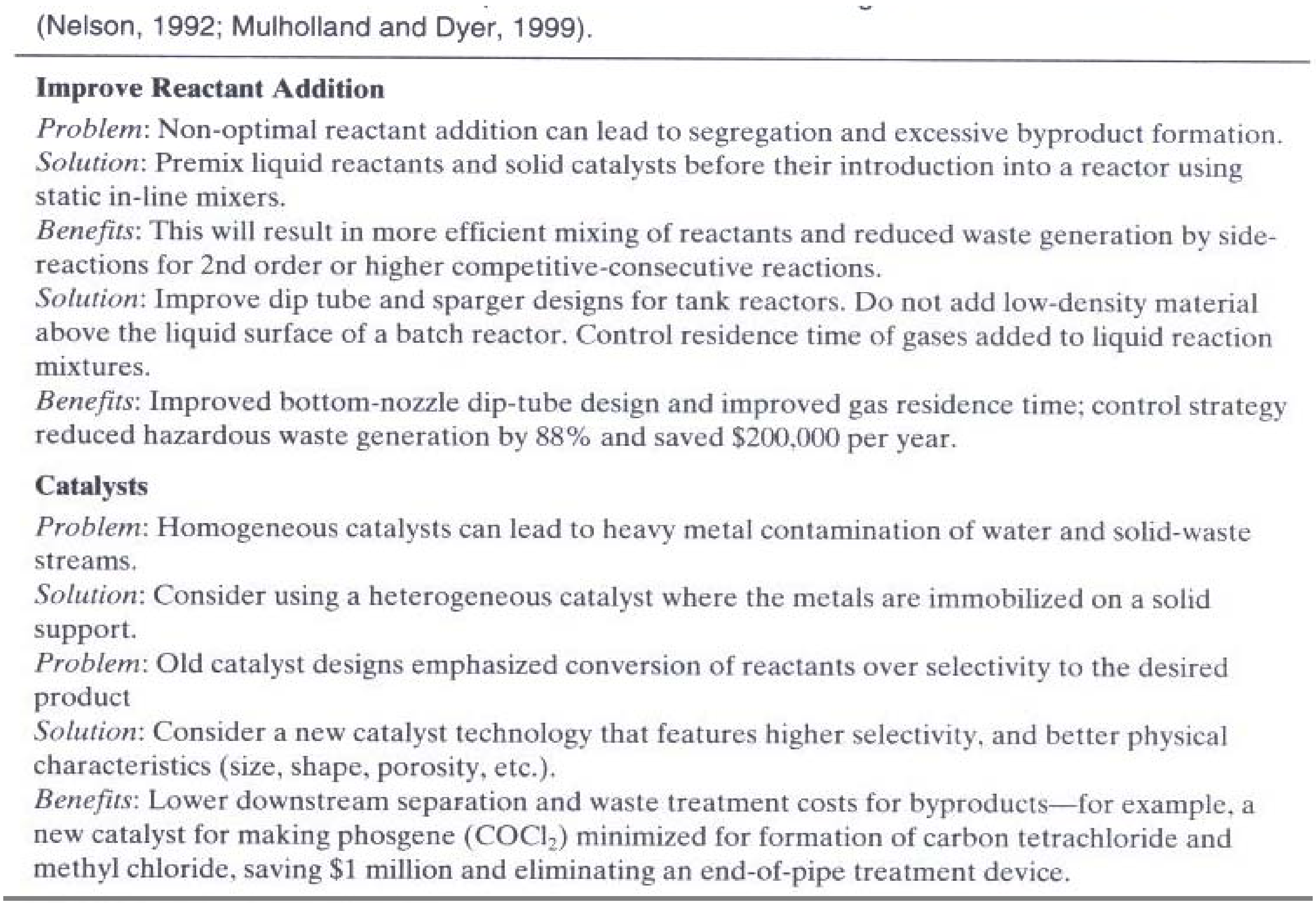
- *If* $n_p > n_w$ *: increasing reactant concentration will increase the selectivity toward the product and away from the waste byproduct*
- *If* $n_p < n_w$ *: increasing reactant concentration will decrease the selectivity toward the desired product*

Summary of other methods

- There are numerous modifications for improving environmental and economic performance of reactors ***(Table 9.3-2)***

Table 9.3-2

Additional reactor operation modifications leading to pollution prevention



(Nelson, 1992; Mulholland and Dyer, 1999).

Improve Reactant Addition

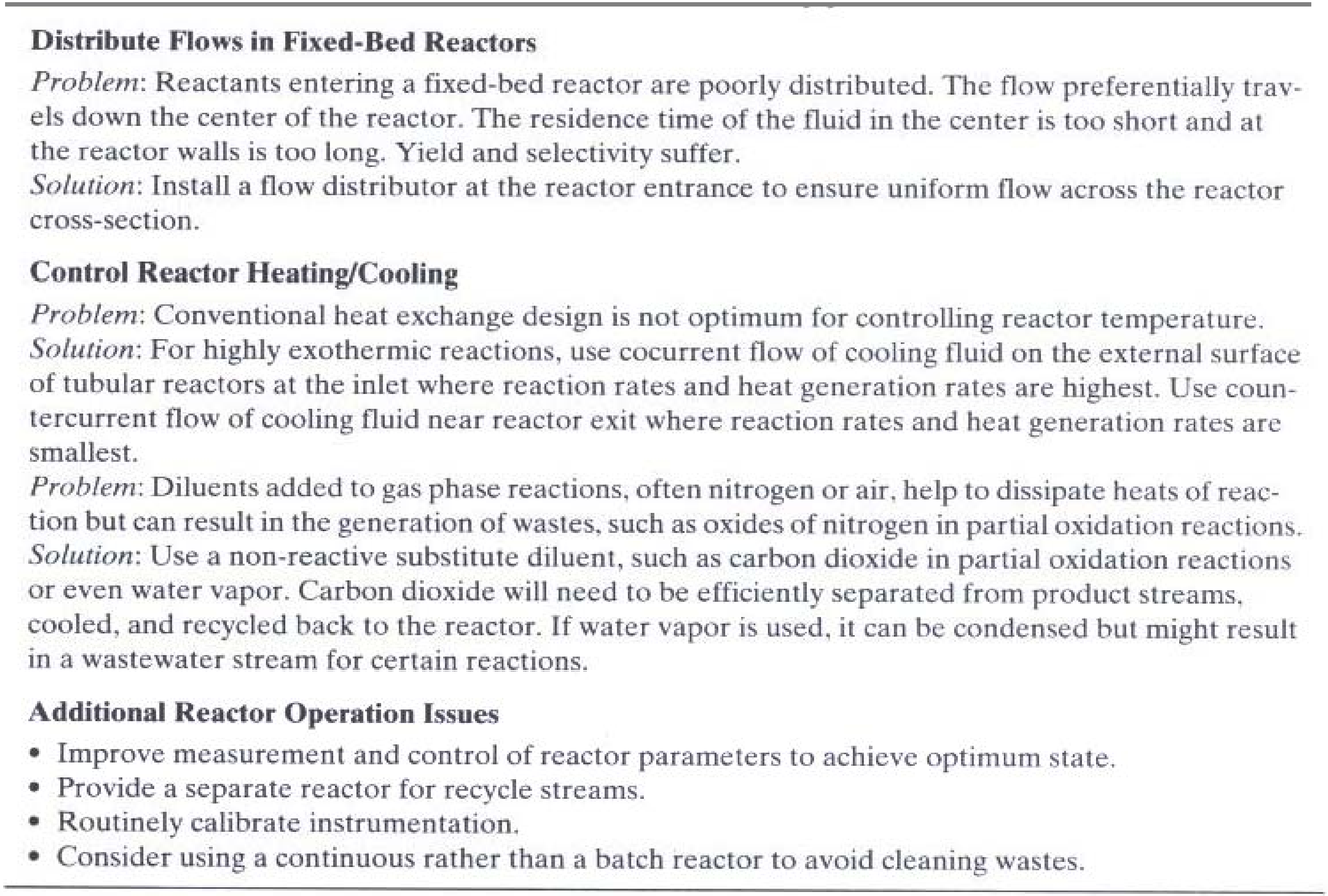
Problem: Non-optimal reactant addition can lead to segregation and excessive byproduct formation.
Solution: Premix liquid reactants and solid catalysts before their introduction into a reactor using static in-line mixers.
Benefits: This will result in more efficient mixing of reactants and reduced waste generation by side-reactions for 2nd order or higher competitive-consecutive reactions.
Solution: Improve dip tube and sparger designs for tank reactors. Do not add low-density material above the liquid surface of a batch reactor. Control residence time of gases added to liquid reaction mixtures.
Benefits: Improved bottom-nozzle dip-tube design and improved gas residence time; control strategy reduced hazardous waste generation by 88% and saved $200,000 per year.

Catalysts

Problem: Homogeneous catalysts can lead to heavy metal contamination of water and solid-waste streams.
Solution: Consider using a heterogeneous catalyst where the metals are immobilized on a solid support.
Problem: Old catalyst designs emphasized conversion of reactants over selectivity to the desired product
Solution: Consider a new catalyst technology that features higher selectivity, and better physical characteristics (size, shape, porosity, etc.).
Benefits: Lower downstream separation and waste treatment costs for byproducts—for example, a new catalyst for making phosgene ($COCl_2$) minimized for formation of carbon tetrachloride and methyl chloride, saving $1 million and eliminating an end-of-pipe treatment device.

Table 9.3-2

Additional reactor operation modifications leading to pollution prevention



Distribute Flows in Fixed-Bed Reactors

Problem: Reactants entering a fixed-bed reactor are poorly distributed. The flow preferentially travels down the center of the reactor. The residence time of the fluid in the center is too short and at the reactor walls is too long. Yield and selectivity suffer.
Solution: Install a flow distributor at the reactor entrance to ensure uniform flow across the reactor cross-section.

Control Reactor Heating/Cooling

Problem: Conventional heat exchange design is not optimum for controlling reactor temperature.
Solution: For highly exothermic reactions, use cocurrent flow of cooling fluid on the external surface of tubular reactors at the inlet where reaction rates and heat generation rates are highest. Use countercurrent flow of cooling fluid near reactor exit where reaction rates and heat generation rates are smallest.
Problem: Diluents added to gas phase reactions, often nitrogen or air, help to dissipate heats of reaction but can result in the generation of wastes, such as oxides of nitrogen in partial oxidation reactions.
Solution: Use a non-reactive substitute diluent, such as carbon dioxide in partial oxidation reactions or even water vapor. Carbon dioxide will need to be efficiently separated from product streams, cooled, and recycled back to the reactor. If water vapor is used, it can be condensed but might result in a wastewater stream for certain reactions.

Additional Reactor Operation Issues

- Improve measurement and control of reactor parameters to achieve optimum state.
- Provide a separate reactor for recycle streams.
- Routinely calibrate instrumentation.
- Consider using a continuous rather than a batch reactor to avoid cleaning wastes.

9.4 Pollution Prevention for Separation Devices

Separation technologies are some of the most common and most important unit operations found in chemical processes. Because feedstocks are often complex mixtures and chemical reactions are not 100% efficient, there is always a need to separate chemical components from one another prior to subsequent processing steps. Separation unit operations generate waste due to their inefficiency, additional energy input, or waste treatment to deal with off-spec products.

In this section, we discuss the use of separation step is presented. Next, design heuristics regarding the use of separation technologies in chemical processes are covered. Finally, we present examples of the use of separation technologies for recovery of valuable components from waste streams, leading eventually to their reuse in the process.

9.4.1 Choice of Mass Separating Agent (MSA)

The correct choice of MSA to employ in a separation technology is an important issue for pollution prevention. A poor choice may result in exposure to toxic substances for not only facility workers but also consumers who use the end product. This is especially important in food products, where exposure to residual agents is by direct ingestion into the body with the food.

Supercritical Fluid Extraction (SFE)

~ *Decaffeinated coffee bean and instant coffees*

~ *Edible oils by volatile solvents*

A poor choice of MSA may lead to excessive energy consumption and the associated health impacts of the emitted criteria pollutants (CO, CO_2, NOx, SOx, particular matter).

9.4.1 Choice of Mass Separating Agent (MSA)

Choice of a mass separating agent (MSA) in an adsorption application can be illustrated using a simple example.

Granular activated carbon (GAC) is a very common type of adsorbent, but for the recovery of metals, it has been found that typical strong cation exchange resins have approximately a 20-fold higher capacity to adsorb Cu^{2+} than GAC. The metal must be recovered from the regenerated adsorbent using a strong acid. In this case, the use of GAC would require more energy consumption and would generate more acid waste than the cation exchange resin.

9.4.2 Process Design and Operation Heuristics for Separation Technologies

★ A typical chemical process can be depicted as shown in Fig. 9.4-1 where reactor converts feeds to products and byproducts that must be separated from each other by the additional input of energy.

★ While it may be impossible or difficult to eliminate all waste streams, there is every reason to be believe that wastes can be minimized

~ by judicious choice of MSA
~ by correct choice and sequencing of separation technologies
~ by careful control of system parameters during operation

Heuristics : 학생으로 하여금 스스로 발견케 하는 학습법

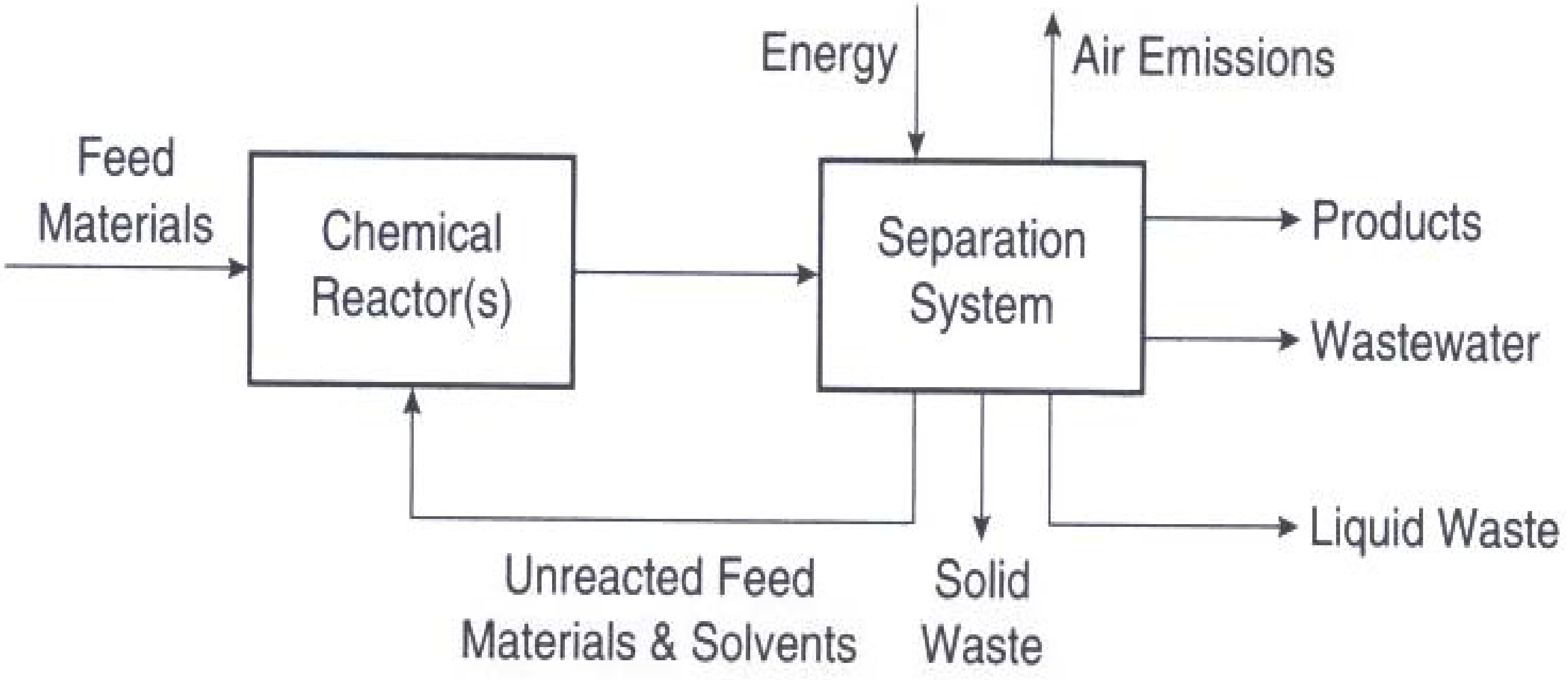


Fig. 9.4-1 *Typical chemical process*

9.4.2 Process Design and Operation Heuristics for Separation Technologies

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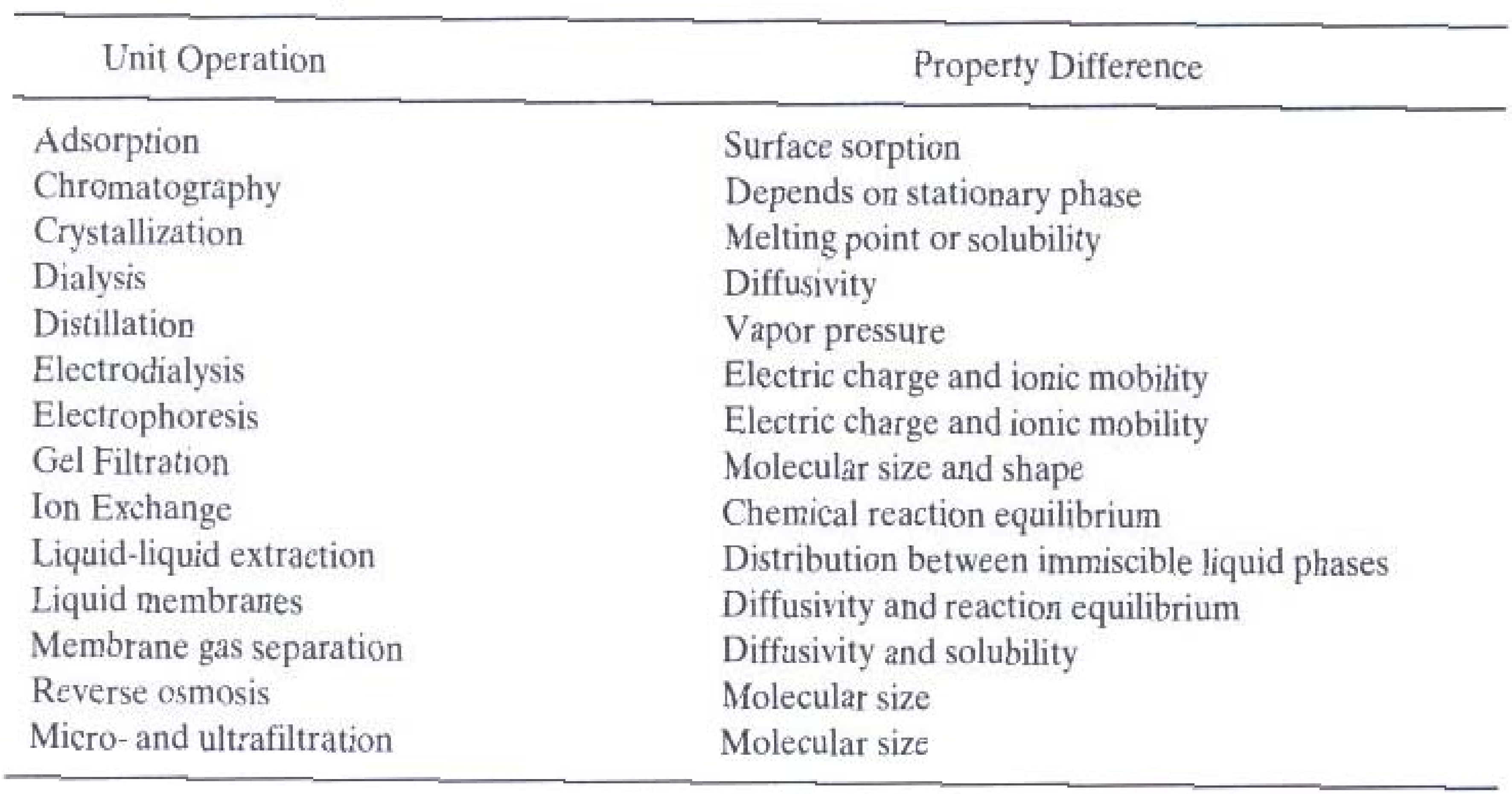
★ Sequencing steps to minimize wastes in separation processes

1. Choose the correct technology
   ~ *based on the physical and chemical properties of molecules to be separated)*
   ~ *generate less waste and use less energy per unit of products* ***(Table 9.4-1)***

2. Consider several pollution prevention heuristics to guide the design of the flowsheet and operation of the units
   (Table 9.4-2 *: Separation heuristics to prevention pollution* ***)***

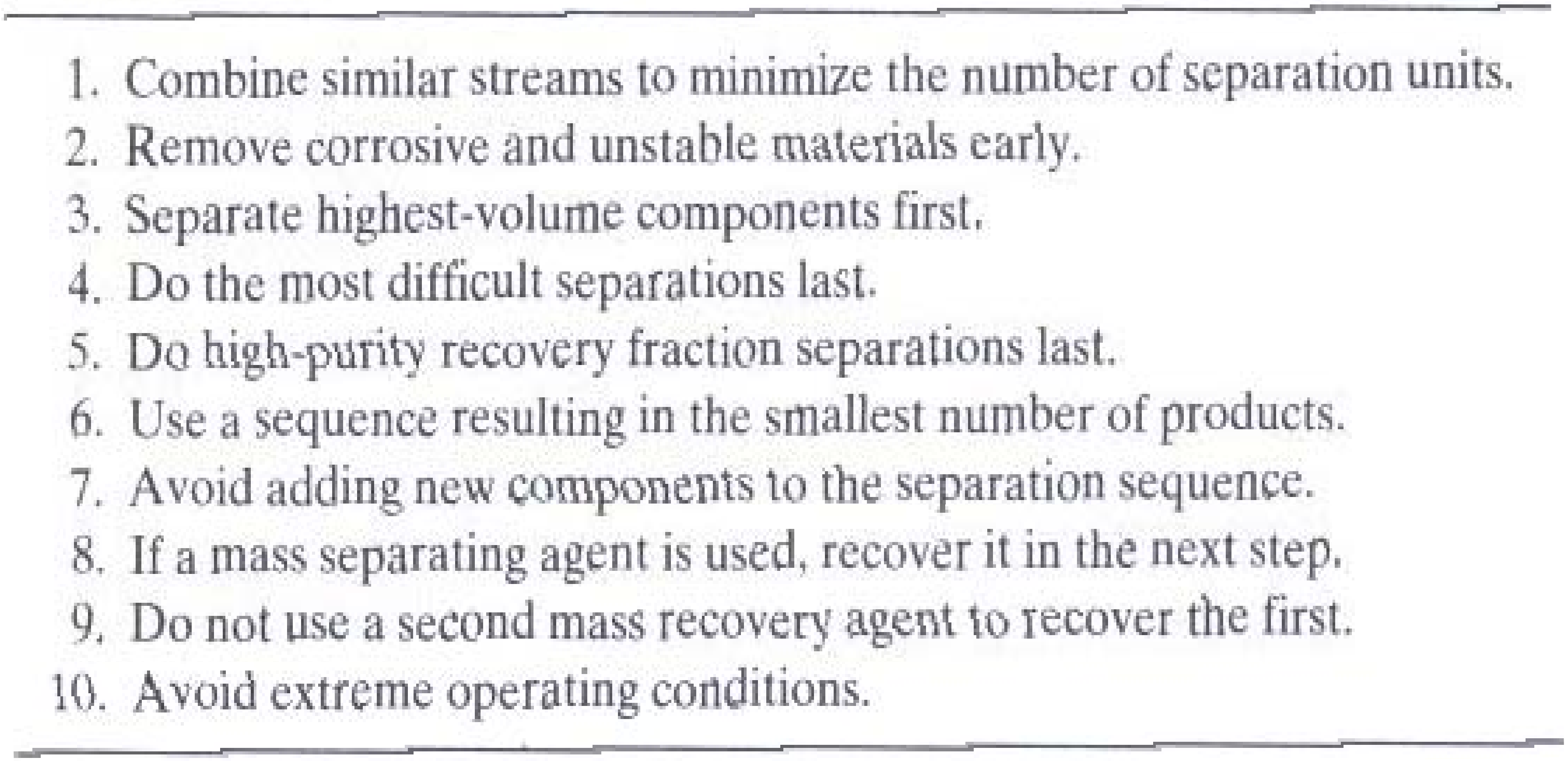
Table 9.4-1
Unit operations for separations and property differences



Unit Operation	Property Difference
Adsorption	Surface sorption
Chromatography	Depends on stationary phase
Crystallization	Melting point or solubility
Dialysis	Diffusivity
Distillation	Vapor pressure
Electrodialysis	Electric charge and ionic mobility
Electrophoresis	Electric charge and ionic mobility
Gel Filtration	Molecular size and shape
Ion Exchange	Chemical reaction equilibrium
Liquid-liquid extraction	Distribution between immiscible liquid phases
Liquid membranes	Diffusivity and reaction equilibrium
Membrane gas separation	Diffusivity and solubility
Reverse osmosis	Molecular size
Micro- and ultrafiltration	Molecular size

Table 9.4-2

Separation heuristics to prevent pollution
(Muholland and Dyer, 1999)



1. Combine similar streams to minimize the number of separation units.
2. Remove corrosive and unstable materials early.
3. Separate highest-volume components first.
4. Do the most difficult separations last.
5. Do high-purity recovery fraction separations last.
6. Use a sequence resulting in the smallest number of products.
7. Avoid adding new components to the separation sequence.
8. If a mass separating agent is used, recover it in the next step.
9. Do not use a second mass recovery agent to recover the first.
10. Avoid extreme operating conditions.

Heuristics : 학생으로 하여금 스스로 발견케 하는 학습법

9.4.2 Process Design and Operation Heuristics for Separation Technologies

★ Pollution prevention example for distillation

Distillation accounts for over 90% of the separation application in chemical processing in the US.

Distillation columns contribute to process waste in 4 major ways

~ *by allowing impurities to remain in a product*
~ *by forming waste within the column itself*
~ *by inadequate condensing of overhead product*
~ *by excessive energy use*

3. Process waste by distillation

- Product impurities above allowable levels must be removed, leading to additional waste streams and energy consumption
- Waste is formed in the reboiler where excessive temperatures and unstable materials combine to form high molecular weight tars or polymers on the heat transfer surface
- Condenser vent must be open to atmosphere to relieve non-condensable gases that build up in the column. If condenser duty is insufficient for internal vapor load, excess vapor will exit the vent as a waste stream
- Energy use leads to the direct release of criteria pollutants (CO, NO_x, SO_x, particular matter, VOC) and global warming gases (primarily CO_2)

3. Example for distillation case

- To increase purity product, reflux ratio must increase
  ~ this increase pressure drop across the column, raise the reboiler temperature, and increase reboiler duty.
  ~ for stable materials, it may be the easiest way to decrease waste generation
  ~ if column is operating close to flooding, reflux ratio is not an option

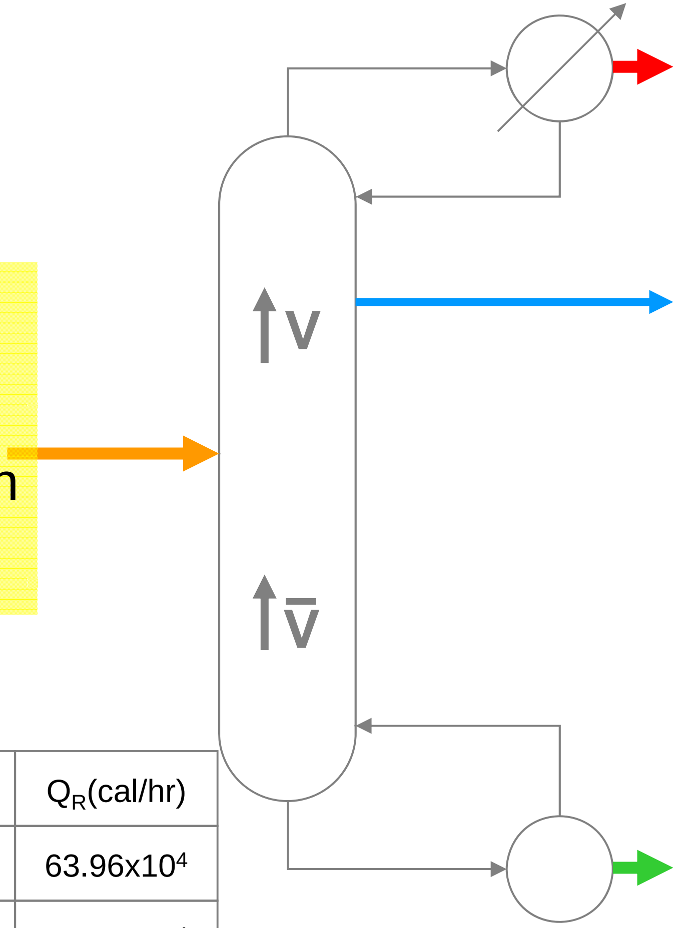
- Replacing existing column internals (trays or packings) with high-efficiency packing results in greater separation for an existing column, and results in both lower pressure drop and reboiler temperature.

- Changing the feed location to the optimum may increase product purity.
  reduce the loss of product to waste (30→1 lb/hr, 20% up capacity, 10% down cooling load, $9,000,000/yr benefit; Mulholland and Dyer, 1999)

- Insulate column, improve feed, reflux, liquid distribution; preheat column feed

- Withdraw product from side stream if overheads product contain light impurity (Example 9.4-1)

Example 9.4-1 Energy saving in ethanol-water distillation: side stream case



Feed

F=100 moles/hr

x_F=0.4 mole fraction

(½ vapor, ½ liquid)

Distillate

D

x_D=0.8 mole fraction

Side Stream

S=20 moles/hr

x_S=0.65 mole fraction

Bottoms

B

x_B=0.02 mole fraction

Column design	L/D	D	$\bar{V}$	Q_R(cal/hr)
Side stream	2.5	32.56	63.96	63.96x10^4
No side stream	2.0	48.72	96.16	96.16x10^4

Using a side stream design, the energy savings are 33.5%

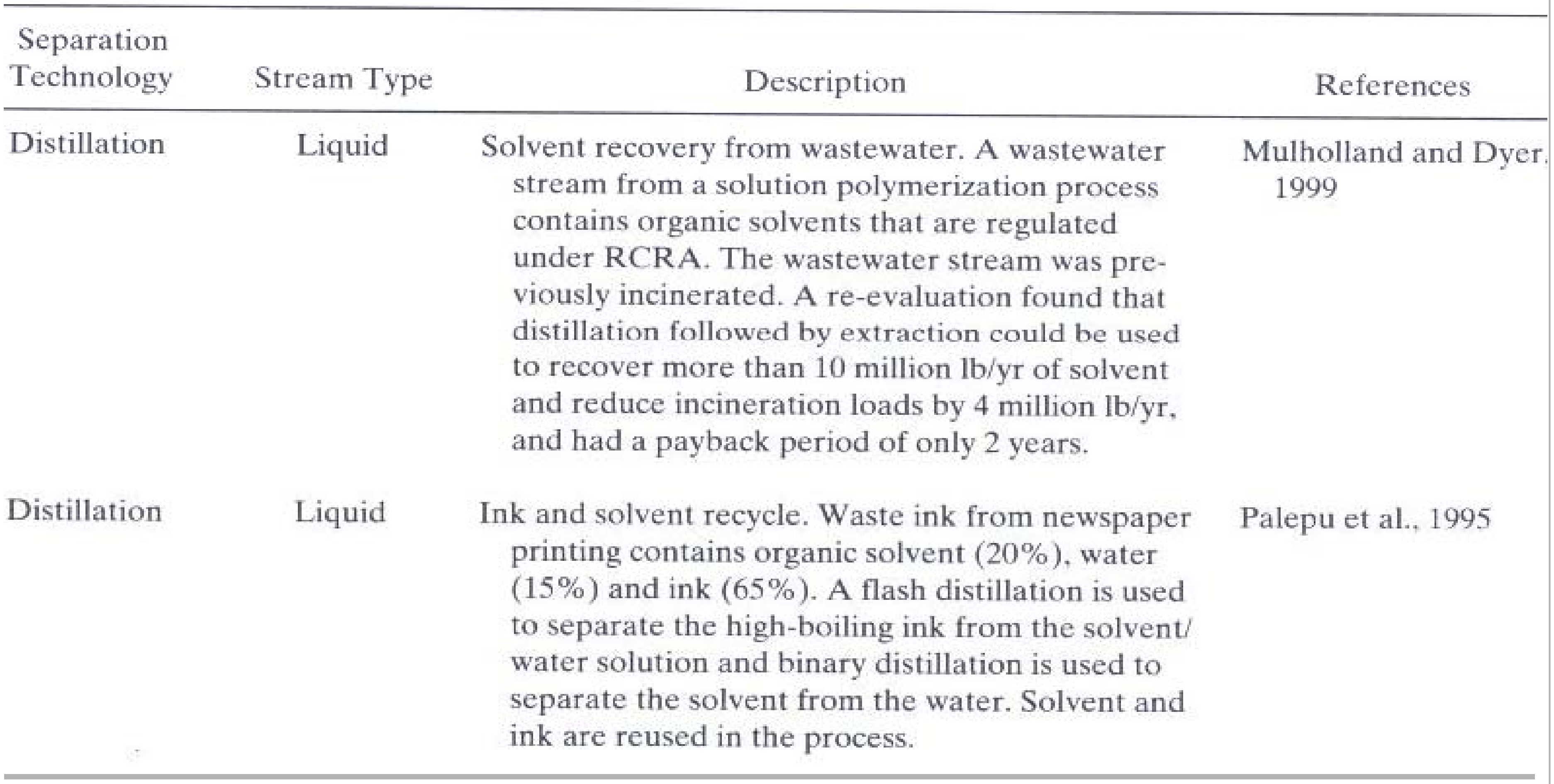
9.4.3 Pollution Prevention Examples for Separations

- Pollution can be prevented using separation processes by selective recovery and reuse of valuable components from waste streams
- Many successful applications of separation technologies for pollution prevention ***(Table 9.4-3)***

9.4.4 Separators with Reactors for Pollution Prevention

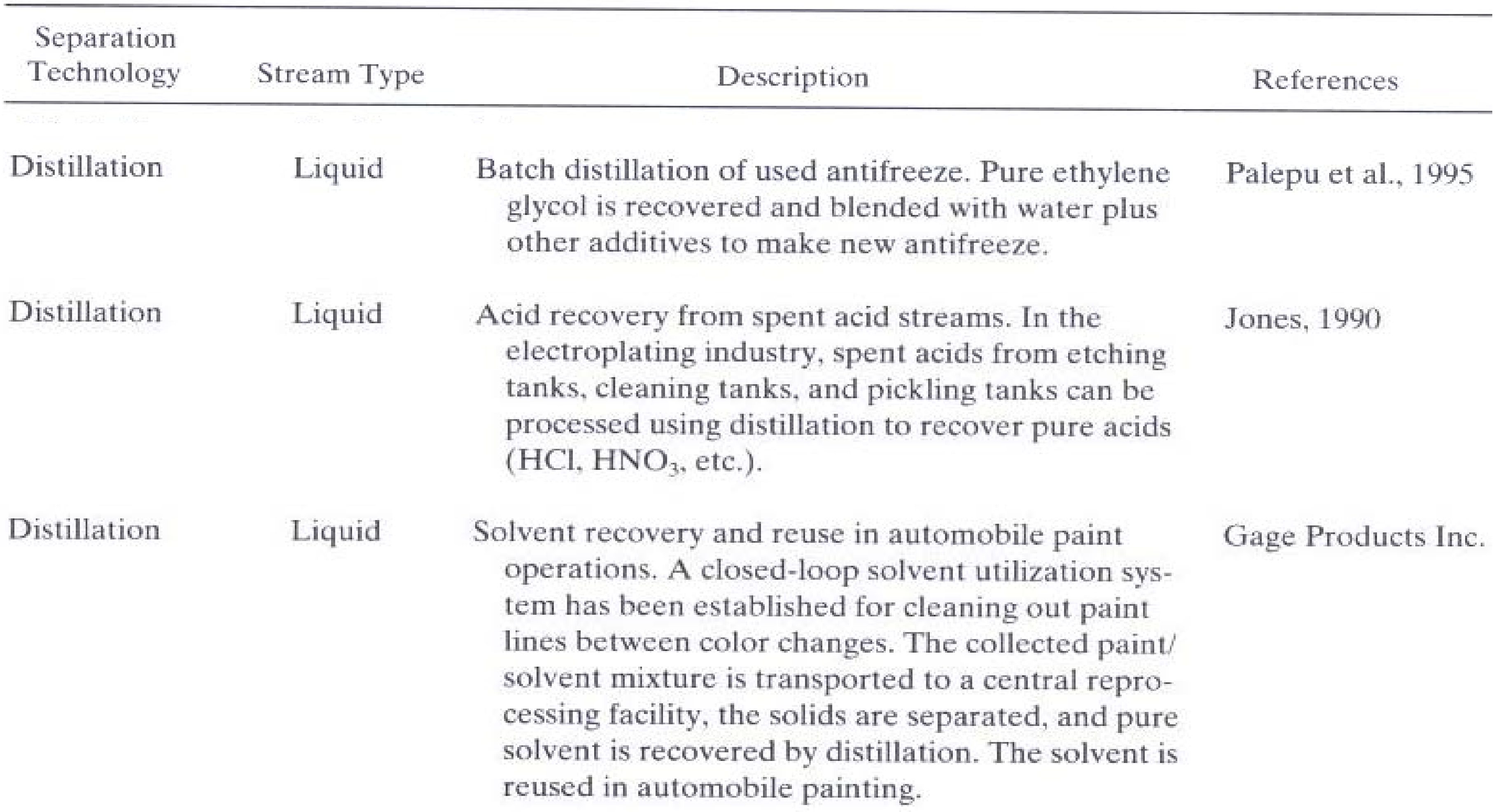
- Separators can be combined with reactors to reduce byproduct generation from reactors and increase reactant conversion to products

Table 9.4-3 *Pollution prevention examples for separation processes*



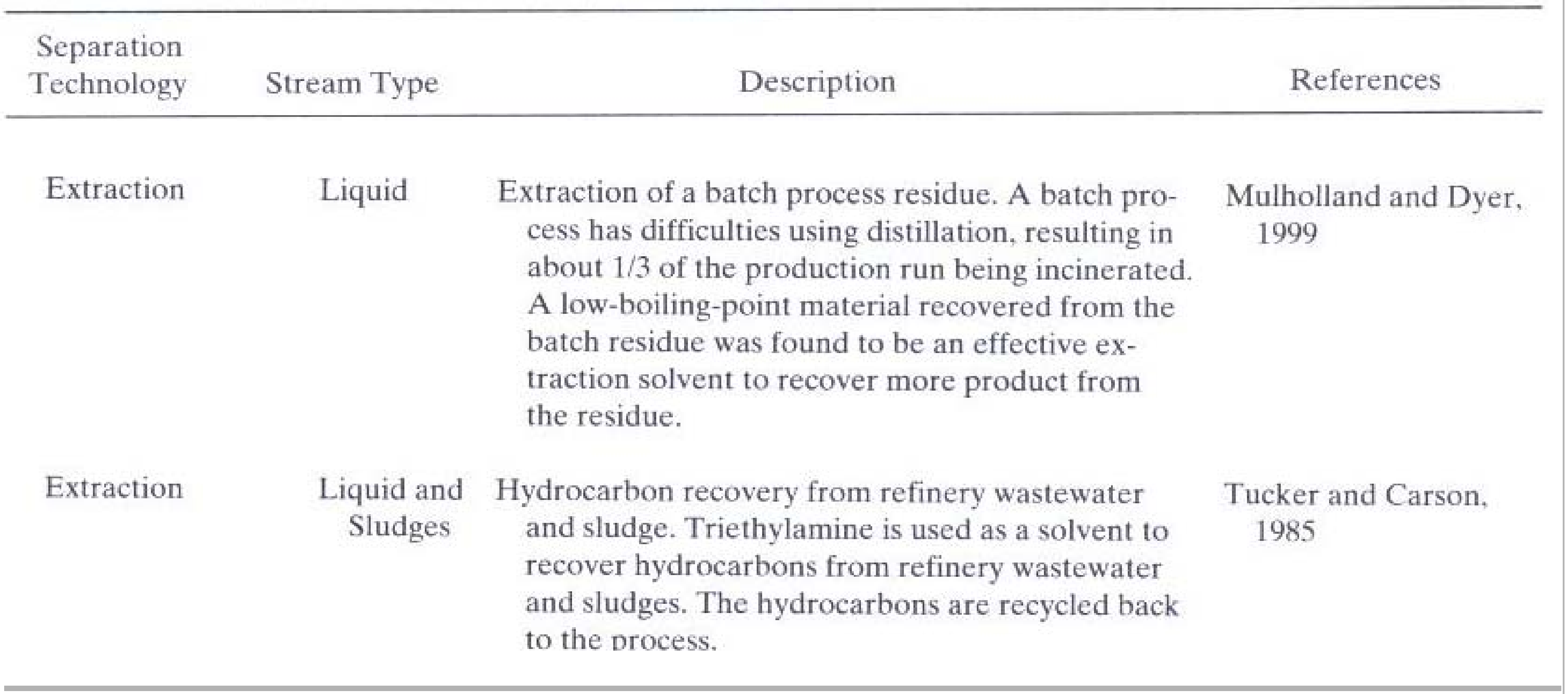
Separation Technology	Stream Type	Description	References
Distillation	Liquid	Solvent recovery from wastewater. A wastewater stream from a solution polymerization process contains organic solvents that are regulated under RCRA. The wastewater stream was previously incinerated. A re-evaluation found that distillation followed by extraction could be used to recover more than 10 million lb/yr of solvent and reduce incineration loads by 4 million lb/yr, and had a payback period of only 2 years.	Mulholland and Dyer, 1999
Distillation	Liquid	Ink and solvent recycle. Waste ink from newspaper printing contains organic solvent (20%), water (15%) and ink (65%). A flash distillation is used to separate the high-boiling ink from the solvent/water solution and binary distillation is used to separate the solvent from the water. Solvent and ink are reused in the process.	Palepu et al., 1995

Table 9.4-3 *Pollution prevention examples for separation processes*



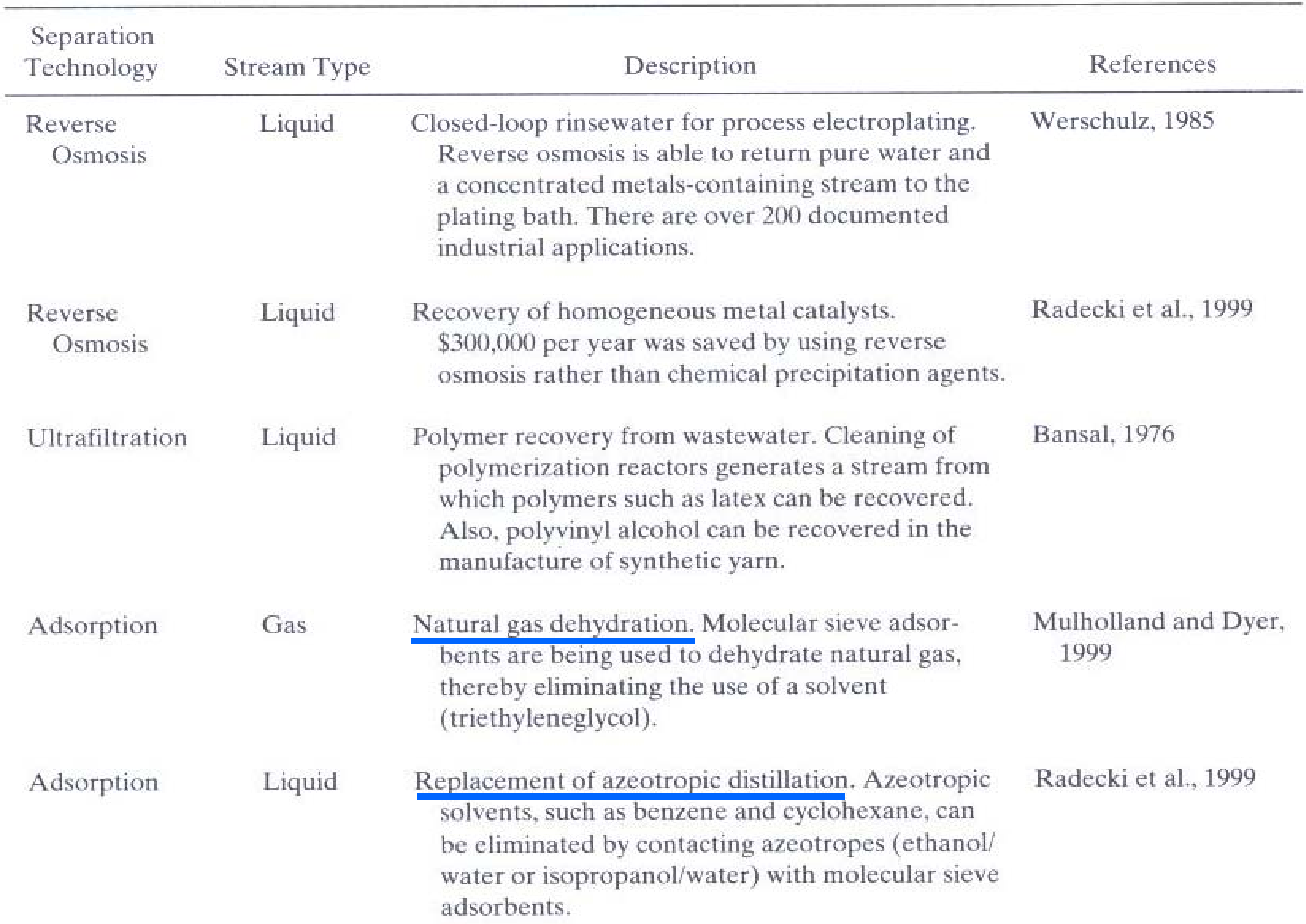
Separation Technology	Stream Type	Description	References
Distillation	Liquid	Batch distillation of used antifreeze. Pure ethylene glycol is recovered and blended with water plus other additives to make new antifreeze.	Palepu et al., 1995
Distillation	Liquid	Acid recovery from spent acid streams. In the electroplating industry, spent acids from etching tanks, cleaning tanks, and pickling tanks can be processed using distillation to recover pure acids (HCl, HNO_3, etc.).	Jones, 1990
Distillation	Liquid	Solvent recovery and reuse in automobile paint operations. A closed-loop solvent utilization system has been established for cleaning out paint lines between color changes. The collected paint/solvent mixture is transported to a central reprocessing facility, the solids are separated, and pure solvent is recovered by distillation. The solvent is reused in automobile painting.	Gage Products Inc.

Table 9.4-3 *Pollution prevention examples for separation processes*



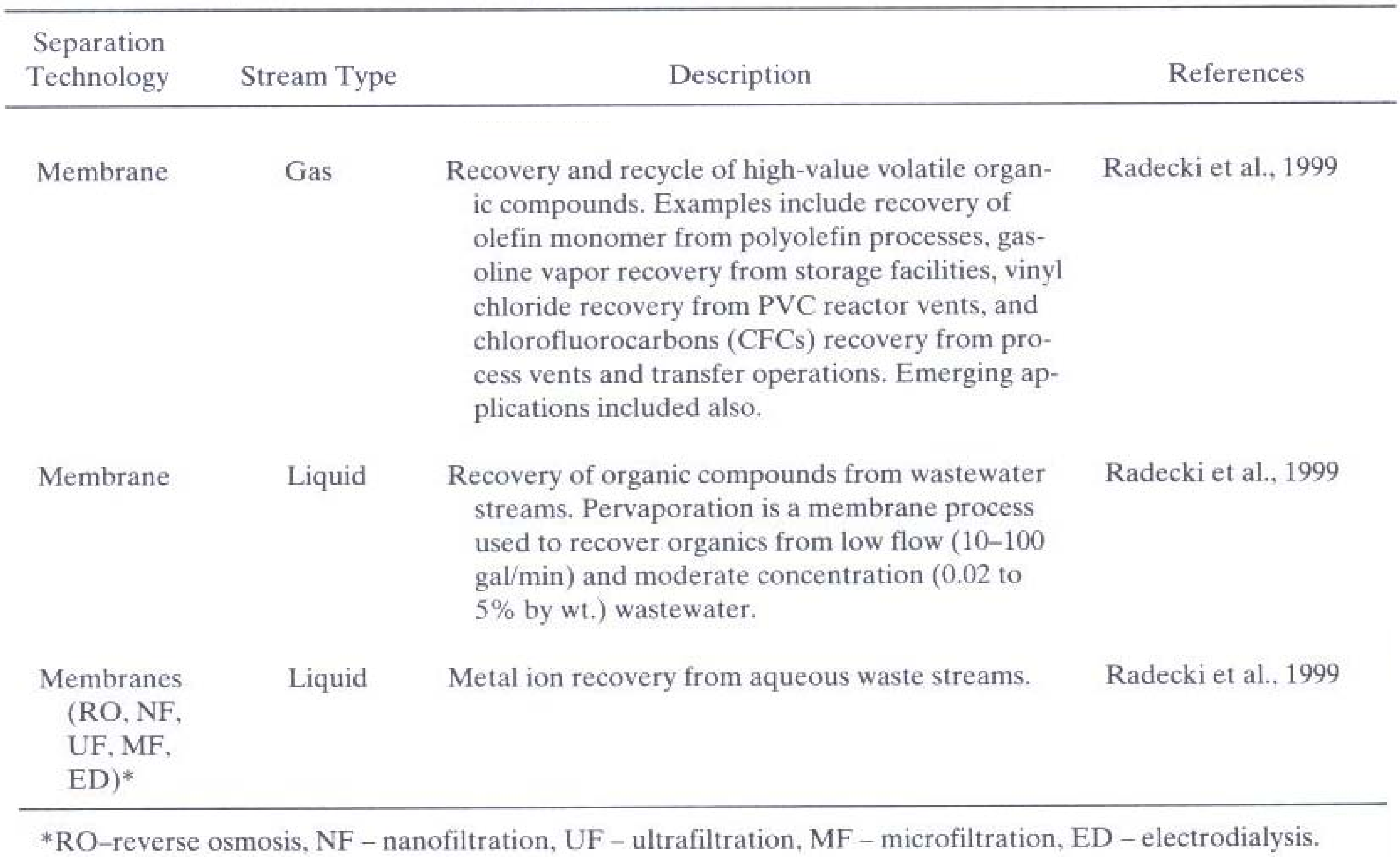
Separation Technology	Stream Type	Description	References
Extraction	Liquid	Extraction of a batch process residue. A batch process has difficulties using distillation, resulting in about 1/3 of the production run being incinerated. A low-boiling-point material recovered from the batch residue was found to be an effective extraction solvent to recover more product from the residue.	Mulholland and Dyer, 1999
Extraction	Liquid and Sludges	Hydrocarbon recovery from refinery wastewater and sludge. Triethylamine is used as a solvent to recover hydrocarbons from refinery wastewater and sludges. The hydrocarbons are recycled back to the process.	Tucker and Carson, 1985

Table 9.4-3 *Pollution prevention examples for separation processes*



Separation Technology	Stream Type	Description	References
Reverse Osmosis	Liquid	Closed-loop rinsewater for process electroplating. Reverse osmosis is able to return pure water and a concentrated metals-containing stream to the plating bath. There are over 200 documented industrial applications.	Werschulz, 1985
Reverse Osmosis	Liquid	Recovery of homogeneous metal catalysts. $300,000 per year was saved by using reverse osmosis rather than chemical precipitation agents.	Radecki et al., 1999
Ultrafiltration	Liquid	Polymer recovery from wastewater. Cleaning of polymerization reactors generates a stream from which polymers such as latex can be recovered. Also, polyvinyl alcohol can be recovered in the manufacture of synthetic yarn.	Bansal, 1976
Adsorption	Gas	Natural gas dehydration. Molecular sieve adsorbents are being used to dehydrate natural gas, thereby eliminating the use of a solvent (triethyleneglycol).	Mulholland and Dyer, 1999
Adsorption	Liquid	Replacement of azeotropic distillation. Azeotropic solvents, such as benzene and cyclohexane, can be eliminated by contacting azeotropes (ethanol/water or isopropanol/water) with molecular sieve adsorbents.	Radecki et al., 1999

Table 9.4-3 *Pollution prevention examples for separation processes*



Separation Technology	Stream Type	Description	References
Membrane	Gas	Recovery and recycle of high-value volatile organic compounds. Examples include recovery of olefin monomer from polyolefin processes, gasoline vapor recovery from storage facilities, vinyl chloride recovery from PVC reactor vents, and chlorofluorocarbons (CFCs) recovery from process vents and transfer operations. Emerging applications included also.	Radecki et al., 1999
Membrane	Liquid	Recovery of organic compounds from wastewater streams. Pervaporation is a membrane process used to recover organics from low flow (10–100 gal/min) and moderate concentration (0.02 to 5% by wt.) wastewater.	Radecki et al., 1999
Membranes (RO, NF, UF, MF, ED)*	Liquid	Metal ion recovery from aqueous waste streams.	Radecki et al., 1999

*RO–reverse osmosis, NF – nanofiltration, UF – ultrafiltration, MF – microfiltration, ED – electrodialysis.

9.5 Pollution Prevention Applications for Separative Reactors

- An exciting new reactor type that has high potential for reducing waste generation

- These hybrid systems combine reaction and separation in a single unit *(requirements for downstream processing units are reduced and leading to lower costs)*

- Key feature is the ability to control the addition of reactants and removal of product more precisely than traditional designs (Example : *Rxn & adsorption of oxidative coupling of* CH_4 *,OCM)*
OCM: Oxidative coupling of methane

9.5 Pollution Prevention Applications for Separative Reactors

OCM (*Oxidative coupling of methane), T=1000K*

$2CH_4 + 1/2\ O_2 \rightarrow C_2H_6 + H_2O$ (Desired)

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$ (Desired)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (Undesired)

- In traditional process (Fixed bed): $CH_4/O_2 = 50$ or more
  high selectivity of C_2 *= 80-90%, low yield of* C_2 *<20%*

- Separative reactor:
  = Fixed bed catalytic reactor + cooler adsorption bed
  yield of C_2 *=50-65%*

Fig. 9.5-1 SCMCR for oxidative coupling of methane

9.5 Pollution Prevention Applications for Separative Reactors

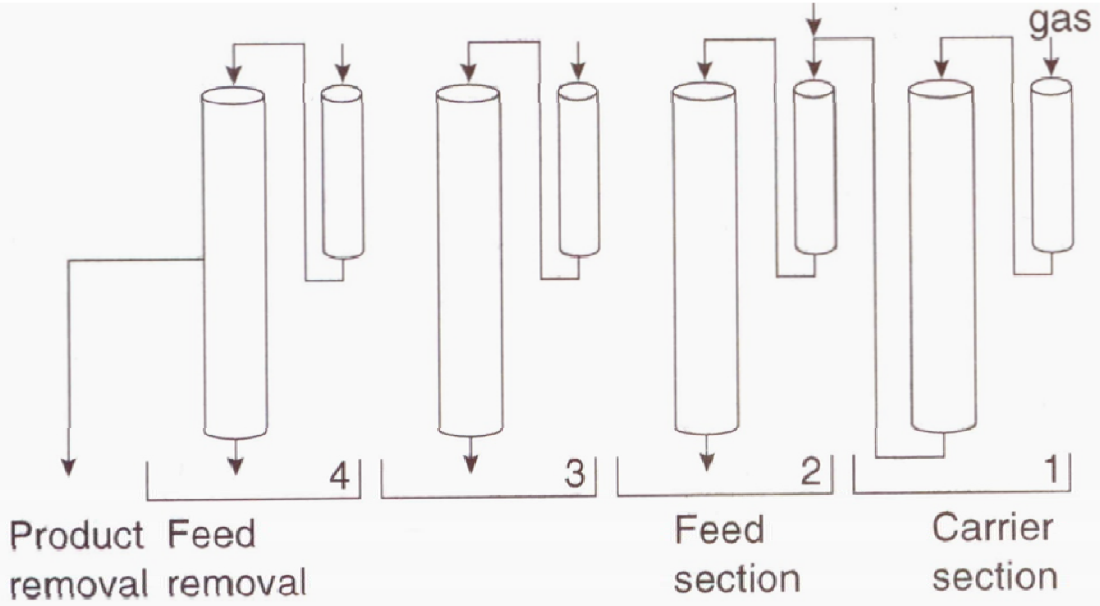


Figure 9.5-1 Schematic of four-section SCMCR for the oxi tive coupling of methane. Adap from Tonkovich et al., 1993.

Fig. 9.5-1 SCMCR for oxidative coupling of methane

9.5 Pollution Prevention Applications for Separative Reactors

Membrane Separative Reactor

- Thermodynamically-limited reactants ($C_6H_{12} \leftrightarrows C_6H_6+3H_2$)

- Parallel reactions in which the product formation has a lower order than byproduct generation

- Series reactions such as selective dehydrogenations and partial oxidations (Ex: ethane oxidative dehydrogenation to ethylene; dehydrogenation of ethylbenzene to produce styrene, conversion 70% compare to traditional 55%)

- Series-parallel reaction

9.6 Pollution Prevention in Storage Tanks and Fugitive Sources

9.6.1 Storage Tank Pollution Prevention

Continual occurrence of air emissions of VOC from roof vents and periodic removal of oil sludge from tank bottoms

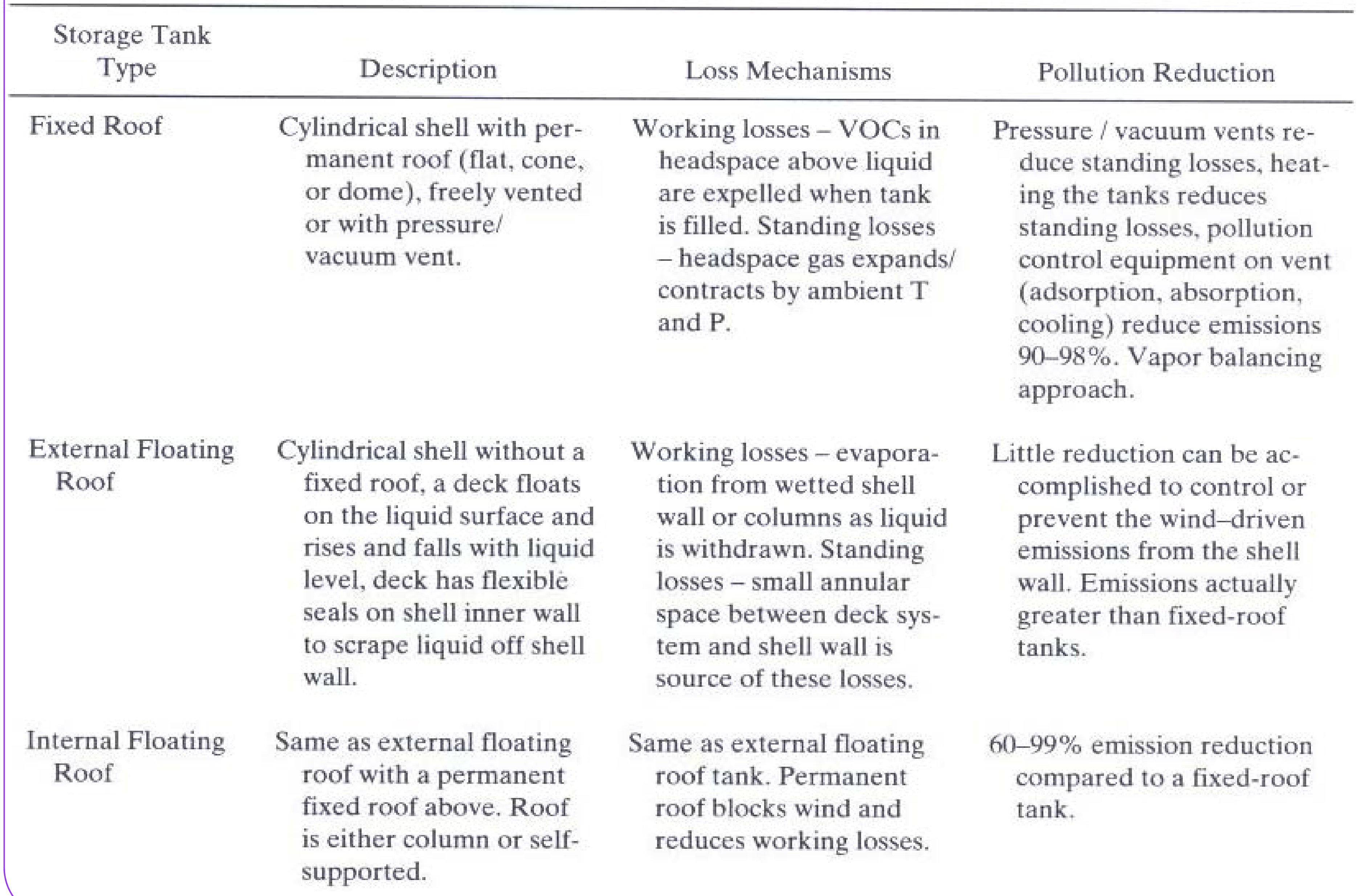
- Tank bottoms are solids or sludges composed of rusts, soil particles, heavy feedstocks, other dense materials.

  various methods dealing with these wastes

  - periodically removed and treated via land application or disposed as hazardous waste
  - preventing sedimentation by action of mixers
  - emulsifying agents
- Air emissions of VOC are major airborne pollution (standing loss and working losses)
  - Emission depends on vapor pressure, geographical location.
  - types of tanks, loss mechanisms and reduction measures

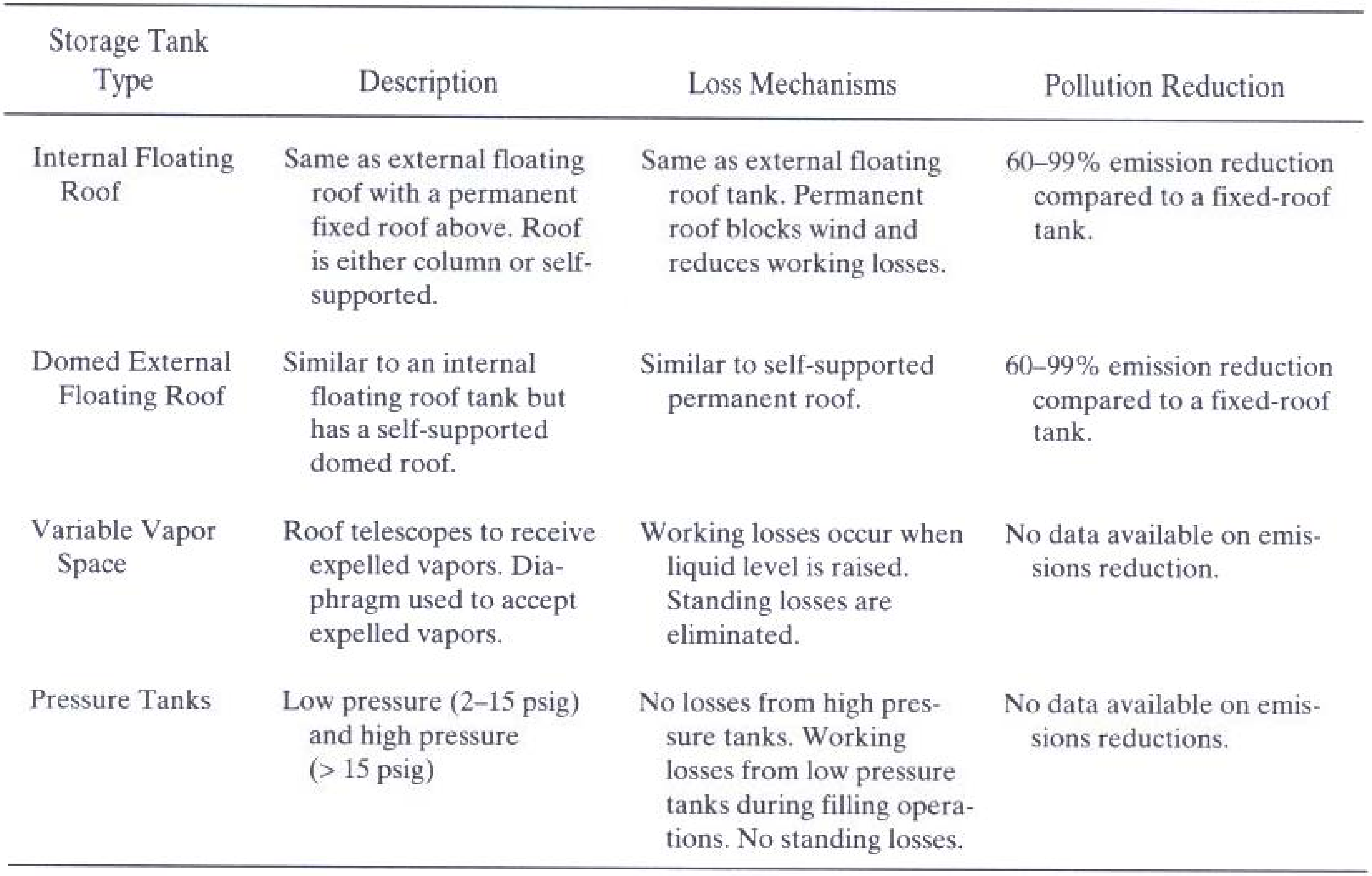
    (Table 9.6-1) (Example 9.6-1)

Table 9.6-1 Storage tank types and pollution reduction strategies

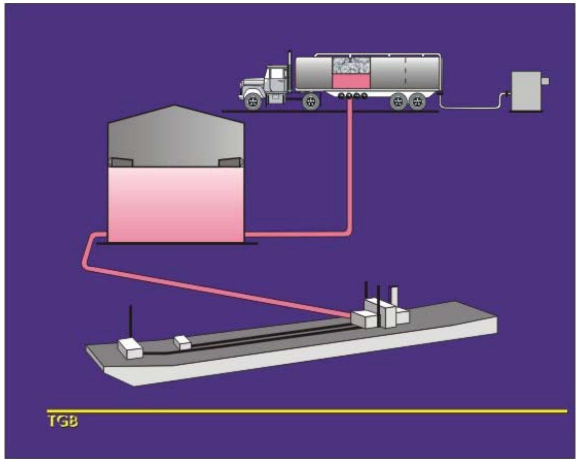


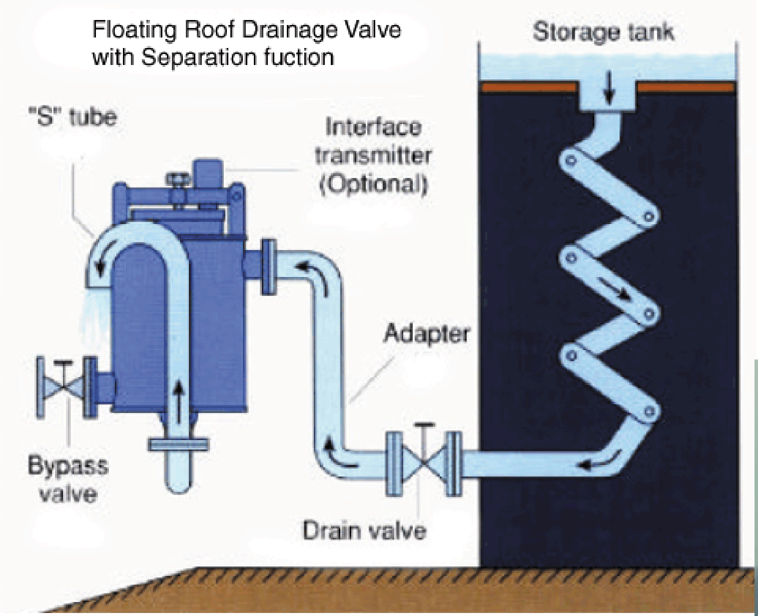
Storage Tank Type	Description	Loss Mechanisms	Pollution Reduction
Fixed Roof	Cylindrical shell with permanent roof (flat, cone, or dome), freely vented or with pressure/ vacuum vent.	Working losses – VOCs in headspace above liquid are expelled when tank is filled. Standing losses – headspace gas expands/ contracts by ambient T and P.	Pressure / vacuum vents reduce standing losses, heating the tanks reduces standing losses, pollution control equipment on vent (adsorption, absorption, cooling) reduce emissions 90–98%. Vapor balancing approach.
External Floating Roof	Cylindrical shell without a fixed roof, a deck floats on the liquid surface and rises and falls with liquid level, deck has flexible seals on shell inner wall to scrape liquid off shell wall.	Working losses – evaporation from wetted shell wall or columns as liquid is withdrawn. Standing losses – small annular space between deck system and shell wall is source of these losses.	Little reduction can be accomplished to control or prevent the wind–driven emissions from the shell wall. Emissions actually greater than fixed-roof tanks.
Internal Floating Roof	Same as external floating roof with a permanent fixed roof above. Roof is either column or self-supported.	Same as external floating roof tank. Permanent roof blocks wind and reduces working losses.	60–99% emission reduction compared to a fixed-roof tank.

Table 9.6-1 Storage tank types and pollution reduction strategies



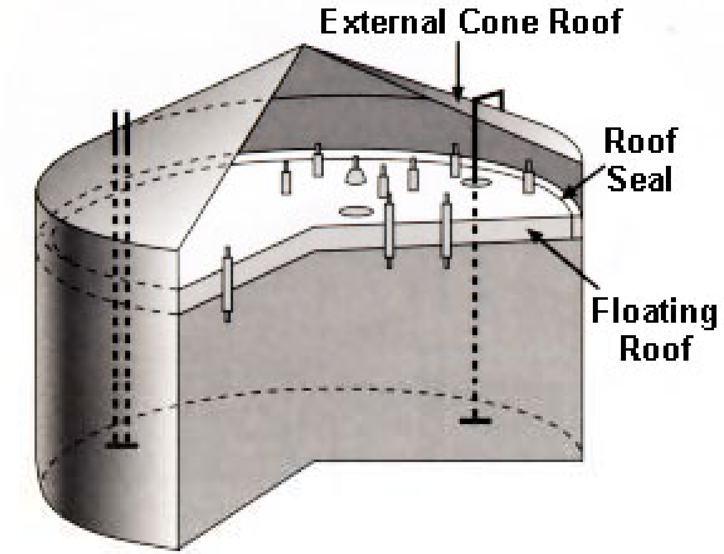
Storage Tank Type	Description	Loss Mechanisms	Pollution Reduction
Internal Floating Roof	Same as external floating roof with a permanent fixed roof above. Roof is either column or self-supported.	Same as external floating roof tank. Permanent roof blocks wind and reduces working losses.	60–99% emission reduction compared to a fixed-roof tank.
Domed External Floating Roof	Similar to an internal floating roof tank but has a self-supported domed roof.	Similar to self-supported permanent roof.	60–99% emission reduction compared to a fixed-roof tank.
Variable Vapor Space	Roof telescopes to receive expelled vapors. Diaphragm used to accept expelled vapors.	Working losses occur when liquid level is raised. Standing losses are eliminated.	No data available on emissions reduction.
Pressure Tanks	Low pressure (2–15 psig) and high pressure (> 15 psig)	No losses from high pressure tanks. Working losses from low pressure tanks during filling operations. No standing losses.	No data available on emissions reductions.

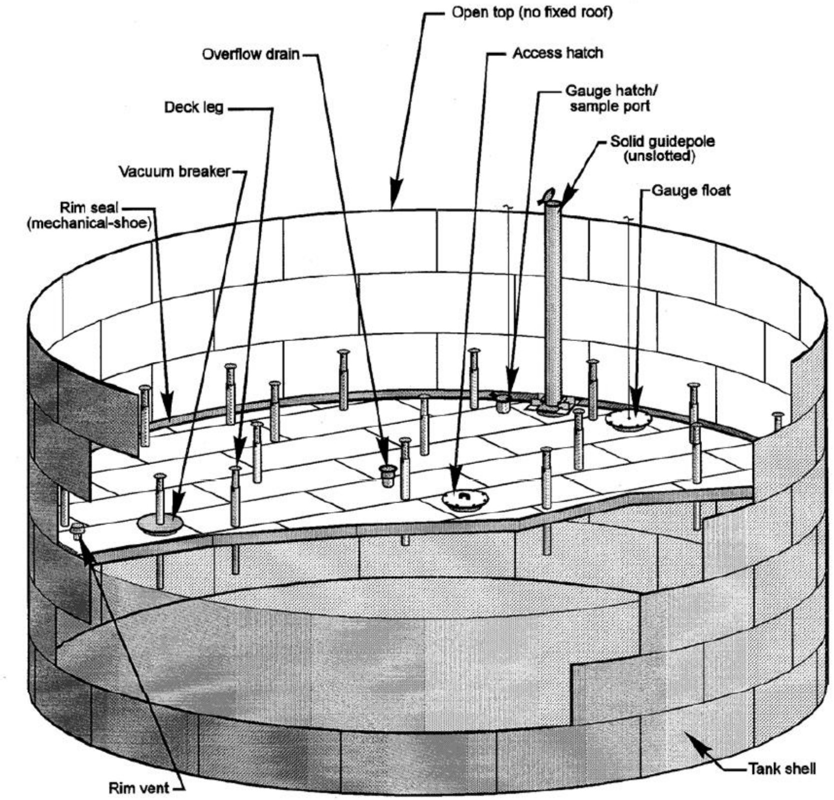

TGB


Floating Roof Drainage Valve
with Separation fuction
Storage tank
"S" tube
Interface
transmitter
(Optional)
Adapter
Bypass
valve
Drain valve

External Floating Roof (EFR)

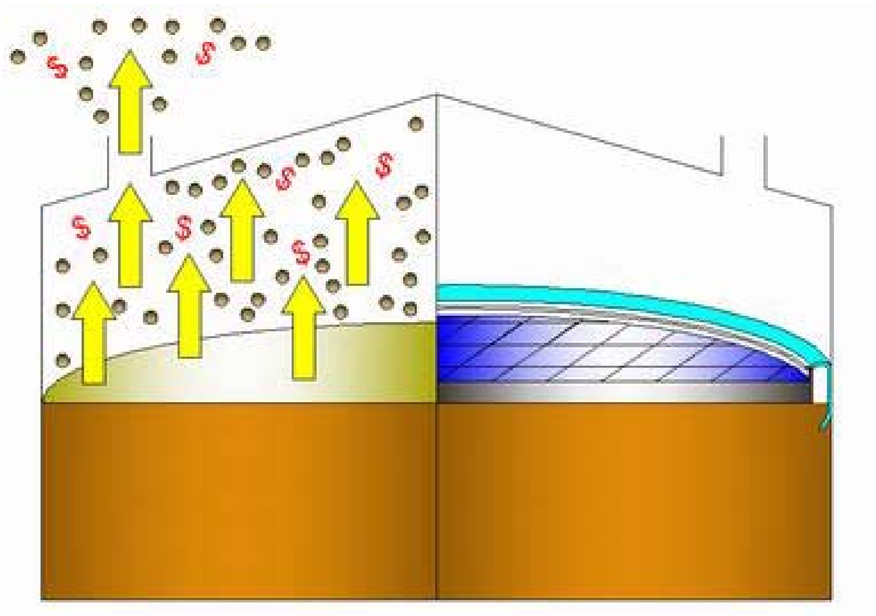
An **external floating roof tank** is a storage tank commonly used to store large quantities of volatile petroleum products such as crude oil or gasoline (petrol). It comprises an open-topped cylindrical steel shell equipped with a roof that floats on the surface of the stored liquid. The roof rises and falls with the liquid level in the tank.

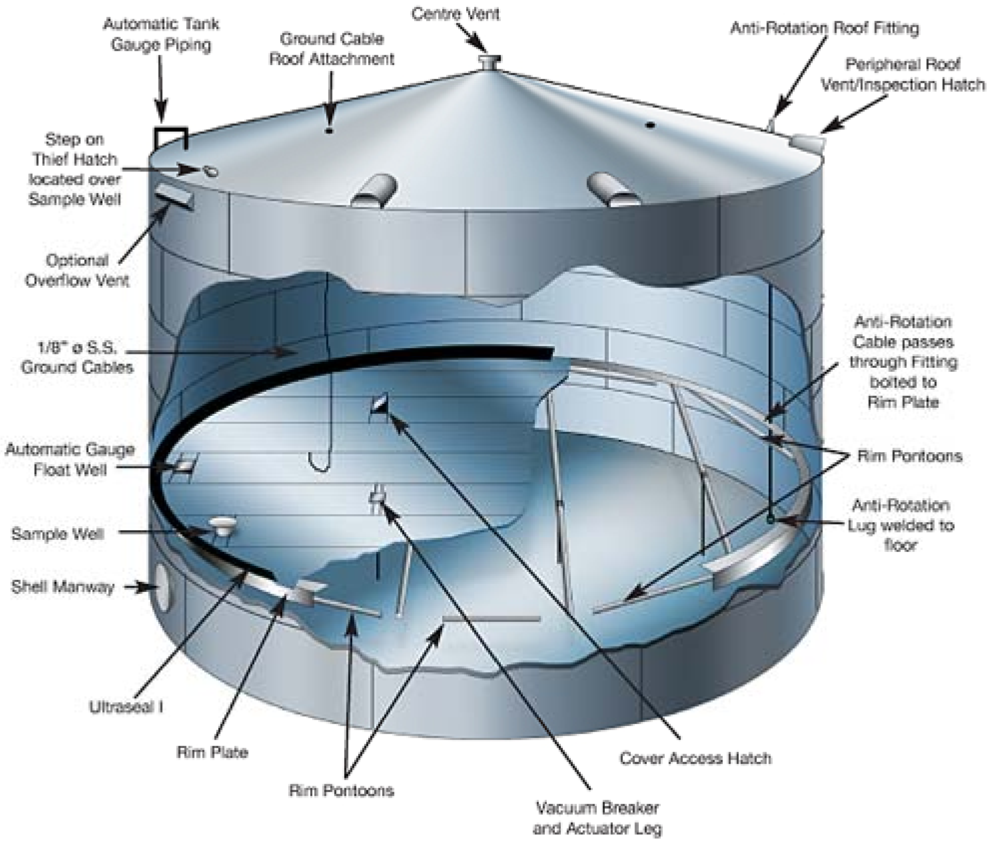




Internal Floating Roof (IFR)

An internal floating roof tank has both a permanent fixed roof and a floating desk inside. The term "deck" or "floating roof" is used in reference to the structure floating on the liquid stored within the tank. The deck of an internal floating roof tank rises and falls with the liquid level whilst in full contact on the underside thus achieving no vapor zone.





9.6.2 Reducing Emissions from Fugitive Sources

- Fugitive emission sources includes valves, pumps, piping connectors, relief valves, sampling connections, compressor seals, open-end lines

- Leaks near seals, valve packings and gaskets are major issues

- Exact timing and location and rate of release is difficult to predict (low-level leaks and episodic sudden leaks)

Fugitive Emission Profiles

- Average rate of emission of VOC from fugitive components of different types can be vary significantly within a given facility

(Demonstration) Estimate emission rate from 2 units at a refinery: a cracking unit and a hydrogen plant **(Table 8.3-3)**

- Equation to calculate emission rate for each component

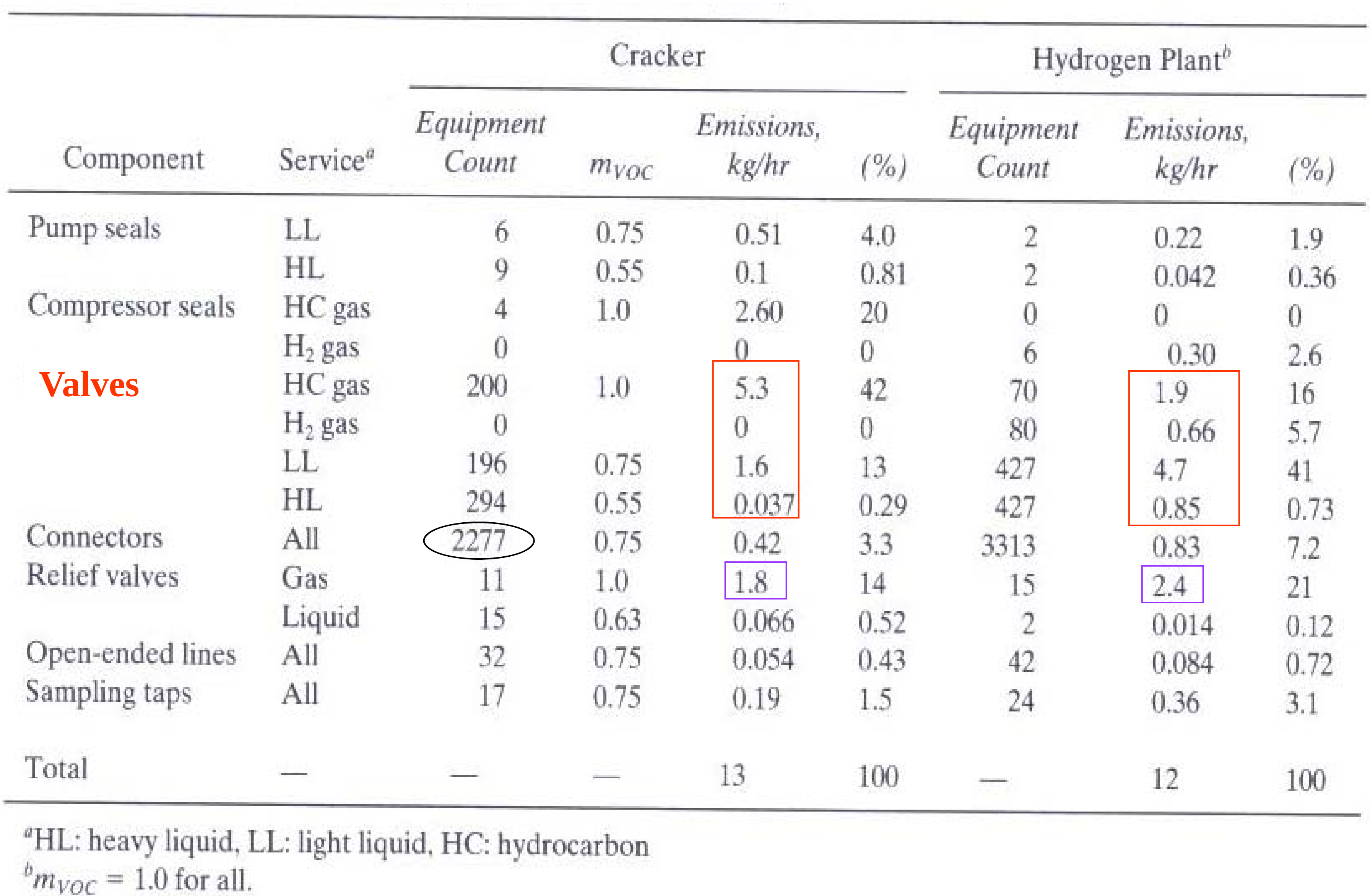
$$\boxed{E = m_{VOC}\, f_{av}}$$

where

E : the emission rate(kg/hr/source),
m_{VOC} : the mass fraction of VOC
f_{av} : the average emission factor

- Fugitive sources and contribution to emission from the 2 processing units are in **Table 9.6-2**

Table 9.6-2 *Distribution of fugitive components and emission rates from a cracking unit and a hydrogen plant at a refinery*



		Cracker				Hydrogen Plant[b]		
Component	Service[a]	*Equipment Count*	m_{VOC}	*Emissions, kg/hr*	*(%)*	*Equipment Count*	*Emissions, kg/hr*	*(%)*
Pump seals	LL	6	0.75	0.51	4.0	2	0.22	1.9
	HL	9	0.55	0.1	0.81	2	0.042	0.36
Compressor seals	HC gas	4	1.0	2.60	20	0	0	0
	H_2 gas	0		0	0	6	0.30	2.6
Valves	HC gas	200	1.0	5.3	42	70	1.9	16
	H_2 gas	0		0	0	80	0.66	5.7
	LL	196	0.75	1.6	13	427	4.7	41
	HL	294	0.55	0.037	0.29	427	0.85	0.73
Connectors	All	2277	0.75	0.42	3.3	3313	0.83	7.2
Relief valves	Gas	11	1.0	1.8	14	15	2.4	21
	Liquid	15	0.63	0.066	0.52	2	0.014	0.12
Open-ended lines	All	32	0.75	0.054	0.43	42	0.084	0.72
Sampling taps	All	17	0.75	0.19	1.5	24	0.36	3.1
Total	—	—	—	13	100	—	12	100

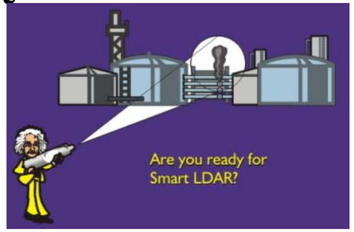
[a] HL: heavy liquid, LL: light liquid, HC: hydrocarbon

[b] m_{VOC} = 1.0 for all.

Methods to Reduce Fugitive Emissions

two methods for reducing or preventing emissions and leaks from fugitive sources

- leak detection & repair (LDAR) of leaking equipment
- equipment modification or replacement with emissionless technologies

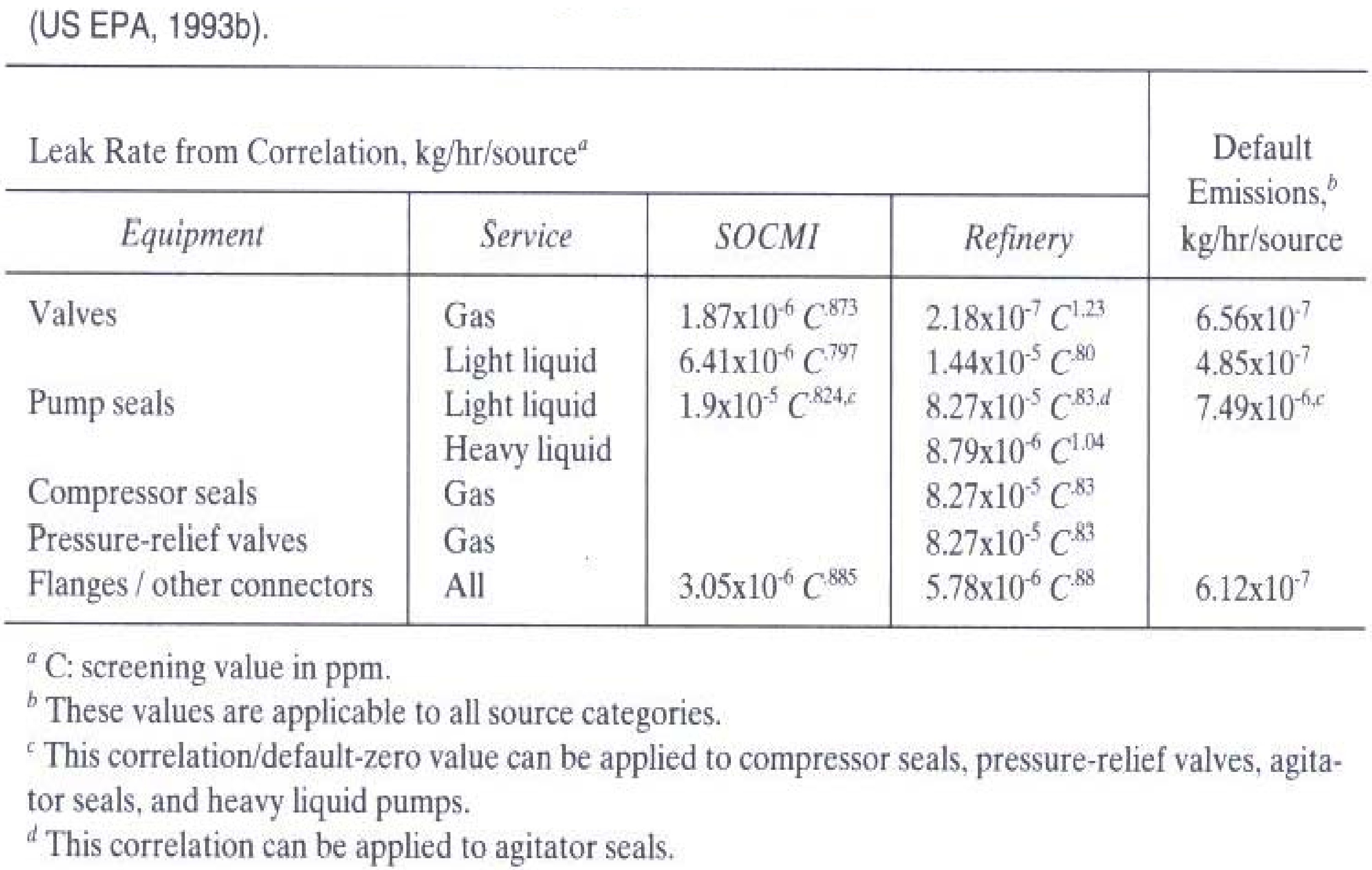


1. LDAR Program to reduce Fugitive Emissions

- equipments *(pump, valve)* are monitored periodically using an organic vapor analyzer *(OVA : it arrow directing to suspected source of leakage, i.e., packing nut on a valve, at a shaft seal on a pump, a gasket, or weld on a flange or connector, etc.)*
- EPA Guidance documents (*if the source registers an OVA reading over a threshold value (>10,000), the equipment is said to be leaking and repair is required)*
- OVA screening values and EPA emission correlations ***(Table 9.6-3)***
- Industrial OVA programs vary greatly in their frequency of monitoring and in their effectiveness

Table 9.6-3

Correlations for estimating fugitive emissions and their default values



(US EPA, 1993b).

Leak Rate from Correlation, kg/hr/source[a]				Default Emissions,[b] kg/hr/source
Equipment	*Service*	*SOCMI*	*Refinery*	
Valves	Gas	$1.87\text{x}10^{-6}\,C^{.873}$	$2.18\text{x}10^{-7}\,C^{1.23}$	$6.56\text{x}10^{-7}$
	Light liquid	$6.41\text{x}10^{-6}\,C^{.797}$	$1.44\text{x}10^{-5}\,C^{.80}$	$4.85\text{x}10^{-7}$
Pump seals	Light liquid	$1.9\text{x}10^{-5}\,C^{.824,c}$	$8.27\text{x}10^{-5}\,C^{.83,d}$	$7.49\text{x}10^{-6,c}$
	Heavy liquid		$8.79\text{x}10^{-6}\,C^{1.04}$	
Compressor seals	Gas		$8.27\text{x}10^{-5}\,C^{.83}$	
Pressure-relief valves	Gas		$8.27\text{x}10^{-5}\,C^{.83}$	
Flanges / other connectors	All	$3.05\text{x}10^{-6}\,C^{.885}$	$5.78\text{x}10^{-6}\,C^{.88}$	$6.12\text{x}10^{-7}$

[a] C: screening value in ppm.

[b] These values are applicable to all source categories.

[c] This correlation/default-zero value can be applied to compressor seals, pressure-relief valves, agitator seals, and heavy liquid pumps.

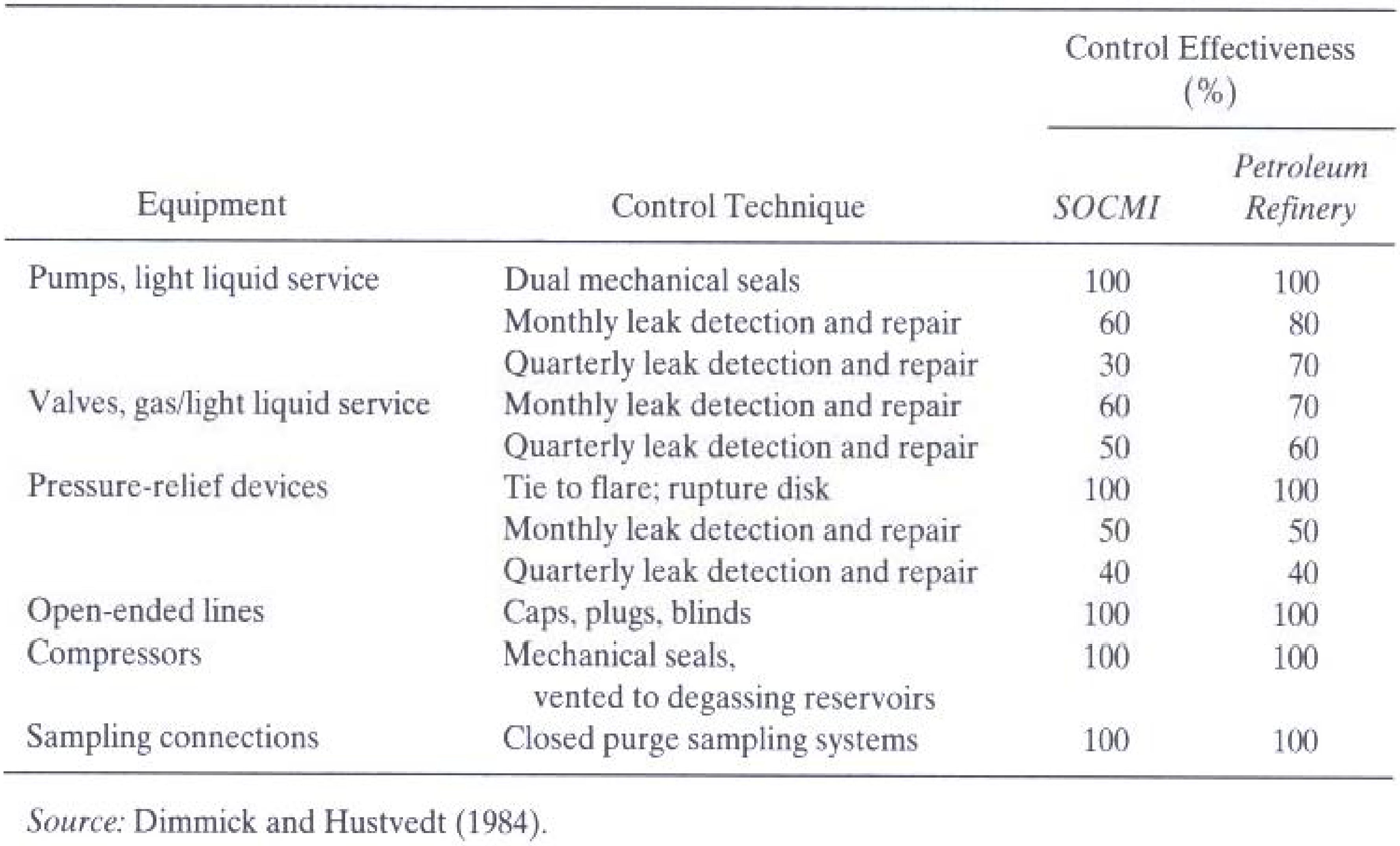
[d] This correlation can be applied to agitator seals.

2. Equipment Modification to Reduce Fugitive Emissions

- Involve redesigning a process so that it has fewer pieces of equipments and connections *(and replacing leaking equipment)*
- Equipment replacement *(valves, connectors, flanges, compressors and pumps)*
- Connectors are the most numerous pieces of equipment *(threaded pipes, couplers, nut-and-ferrule types, etc.)*
- Seals around moving parts are common locations of leaks for fugitive sources
- Emissions control effectiveness of various emission reduction measure ***(Table 9.6-4)***
- Leakless technologies are 100 % effective in eliminating emissions, but are very expensive to purchase and maintain *(10 times than LDAR cost)*
- Fugitive emission in petroleum refinery can be reduced
  - *~ 70 % by using most effective reduction techniques*
  - *~ 60-70 % for SOCMI (Synthetic Organic Chemical Manufacturing Industry) facilities*

Table 9.6-4

Effectiveness of various fugitive emission reduction techniques



Equipment	Control Technique	Control Effectiveness (%) *SOCMI*	Control Effectiveness (%) *Petroleum Refinery*
Pumps, light liquid service	Dual mechanical seals	100	100
	Monthly leak detection and repair	60	80
	Quarterly leak detection and repair	30	70
Valves, gas/light liquid service	Monthly leak detection and repair	60	70
	Quarterly leak detection and repair	50	60
Pressure-relief devices	Tie to flare; rupture disk	100	100
	Monthly leak detection and repair	50	50
	Quarterly leak detection and repair	40	40
Open-ended lines	Caps, plugs, blinds	100	100
Compressors	Mechanical seals, vented to degassing reservoirs	100	100
Sampling connections	Closed purge sampling systems	100	100

Source: Dimmick and Hustvedt (1984).

9.7 Pollution Prevention Assessment Integrated with HAZ-OP Analysis

(The hazard and operability study is a formal procedure to identify potential hazards)

❁ HAZ-OP is a procedure *(identify potential hazards, investigate cause and define the consequences)*

❁ The study is apply to existing process units to improve safety performance. The HAZ-OP method is to apply a series of guide words to the process design intention

❁ *Example of process intention*

- *cooling water flow through a reactor or distillation condensers*
- *inerting system for a reactor, separator, or storage tank*
- *air supply for pneumatically-driven process control valves*

9.7 Pollution Prevention Assessment Integrated with HAZ-OP Analysis

- Guide words associated with the process intentions *(Table 9.7-1)*

- guideword, "**NO**" in the process intention, "cooling water flow through a reactor" indicate a loss of cooling water.

Consequence : *overheated reactor, run-away reaction of explosion*

- It can be applied to unit to whole process
  (Example 9.7-1) also check, (Table 9.7-2)

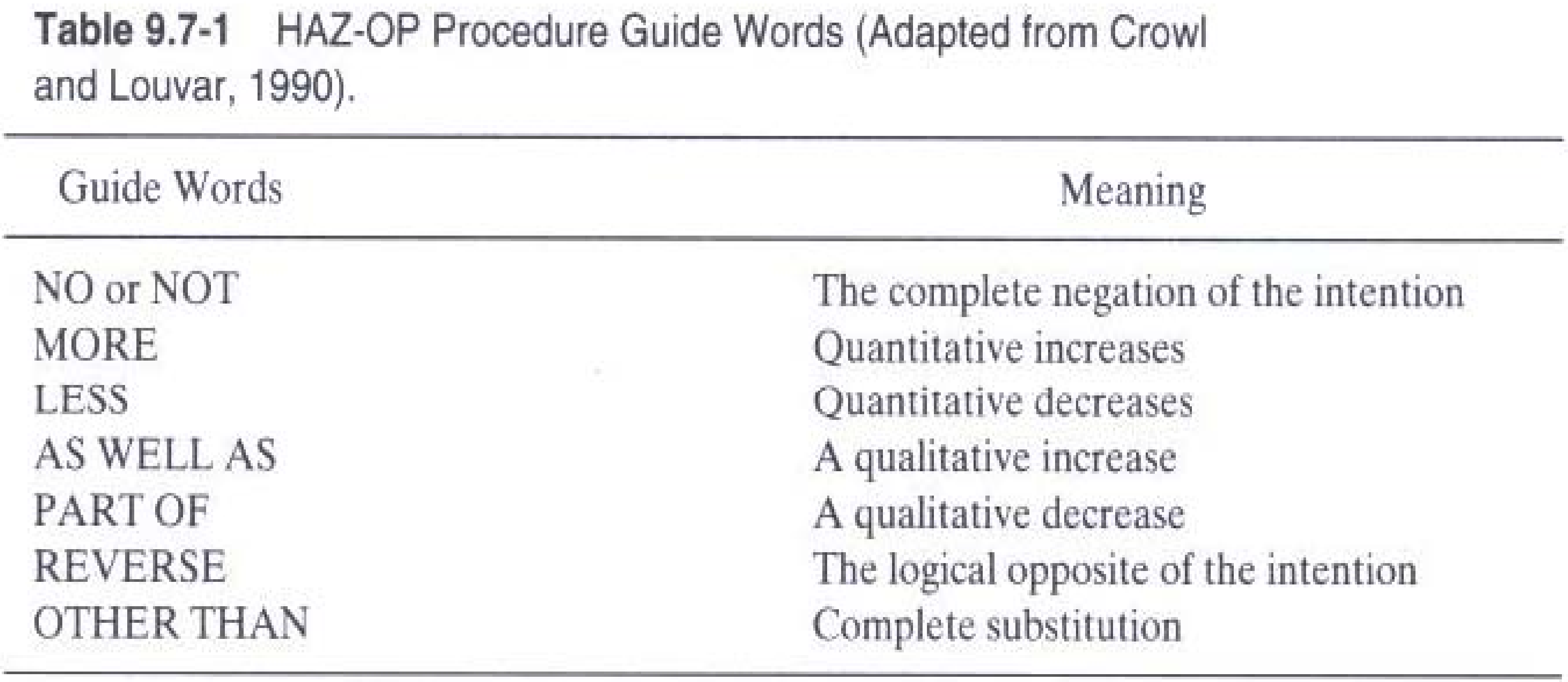
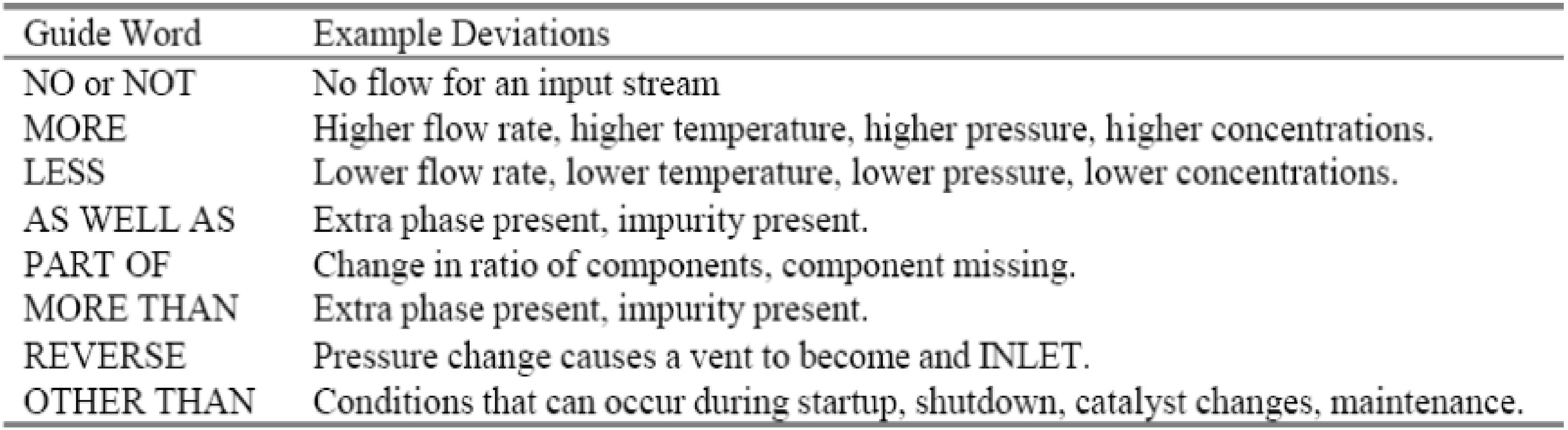


Table 9.7-1 HAZ-OP Procedure Guide Words (Adapted from Crowl and Louvar, 1990).

Guide Words	Meaning
NO or NOT	The complete negation of the intention
MORE	Quantitative increases
LESS	Quantitative decreases
AS WELL AS	A qualitative increase
PART OF	A qualitative decrease
REVERSE	The logical opposite of the intention
OTHER THAN	Complete substitution

HAZ-OP Analysis in Storage tank



Guide Word	Example Deviations
NO or NOT	No flow for an input stream
MORE	Higher flow rate, higher temperature, higher pressure, higher concentrations.
LESS	Lower flow rate, lower temperature, lower pressure, lower concentrations.
AS WELL AS	Extra phase present, impurity present.
PART OF	Change in ratio of components, component missing.
MORE THAN	Extra phase present, impurity present.
REVERSE	Pressure change causes a vent to become and INLET.
OTHER THAN	Conditions that can occur during startup, shutdown, catalyst changes, maintenance.

9.8 Integrating Risk Assessment with Process Design

A Case Study

Thus far in Chapter 9, we have incorporated environmental, health, and safety concerns into the design and unit operations. We have used quantitative assessment measures only to a limited extent. It is very useful to provide a more quantitative risk assessment capability for the evaluation and optimization of unit operations. To this end, a screening-level risk assessment method presented in Chapter 8.

One important application could be screening of byproducts generated in a chemical reactor. Decision regarding optimum reactor operation can then be made based on the risks posed by the individual byproducts generated rather than on just the mass rate of generation for each component. The case study deals with choosing residence time in a fluidized bed reactor for the production of acrylonitrile

9.8 Integrating Risk Assessment with Process Design

A Case Study

Case study: Screening byproducts generated in a chemical reactor :

case study deals with choosing residence time in a fluidized bed reactor for the production of acrylonitrile; Acrylonitrile Reactor Risk-based Input-Output Analysis of a Fluidized Bed Reactor with Catalyst (Bi-Mo-O)

- Ammonoxidation for main acrylonitrile reaction

$$CH_2{=}CH\text{-}CH_3 + NH_3 + 3/2O_2 \rightarrow CH_2{=}CH\text{-}CN + 3H_2O$$

9.8 Integrating Risk Assessment with Process Design
A Case Study

- Ammonoxidation for main acrylonitrile reaction

$CH_2{=}CH\text{-}CH_3 + NH_3 + 3/2O_2 \rightarrow CH_2{=}CH\text{-}CN + 3H_2O$

propylene

acrylonitrile

- possible side reactions

$CH_2{=}CH\text{-}CH_3 + O_2 \rightarrow CH_2{=}CH\text{-}CHO + H_2O$

acrolein

$CH_2{=}CH\text{-}CH_3 + NH_3 + 9/4O_2 \rightarrow CH_3\text{-}CN + 1/2CO_2 + 1/2CO + 3H_2O$

acetonitrile

$CH_2{=}CH\text{-}CHO + NH_3 + 1/2O_2 \rightarrow CH_2{=}CH\text{-}CN + 2H_2O$

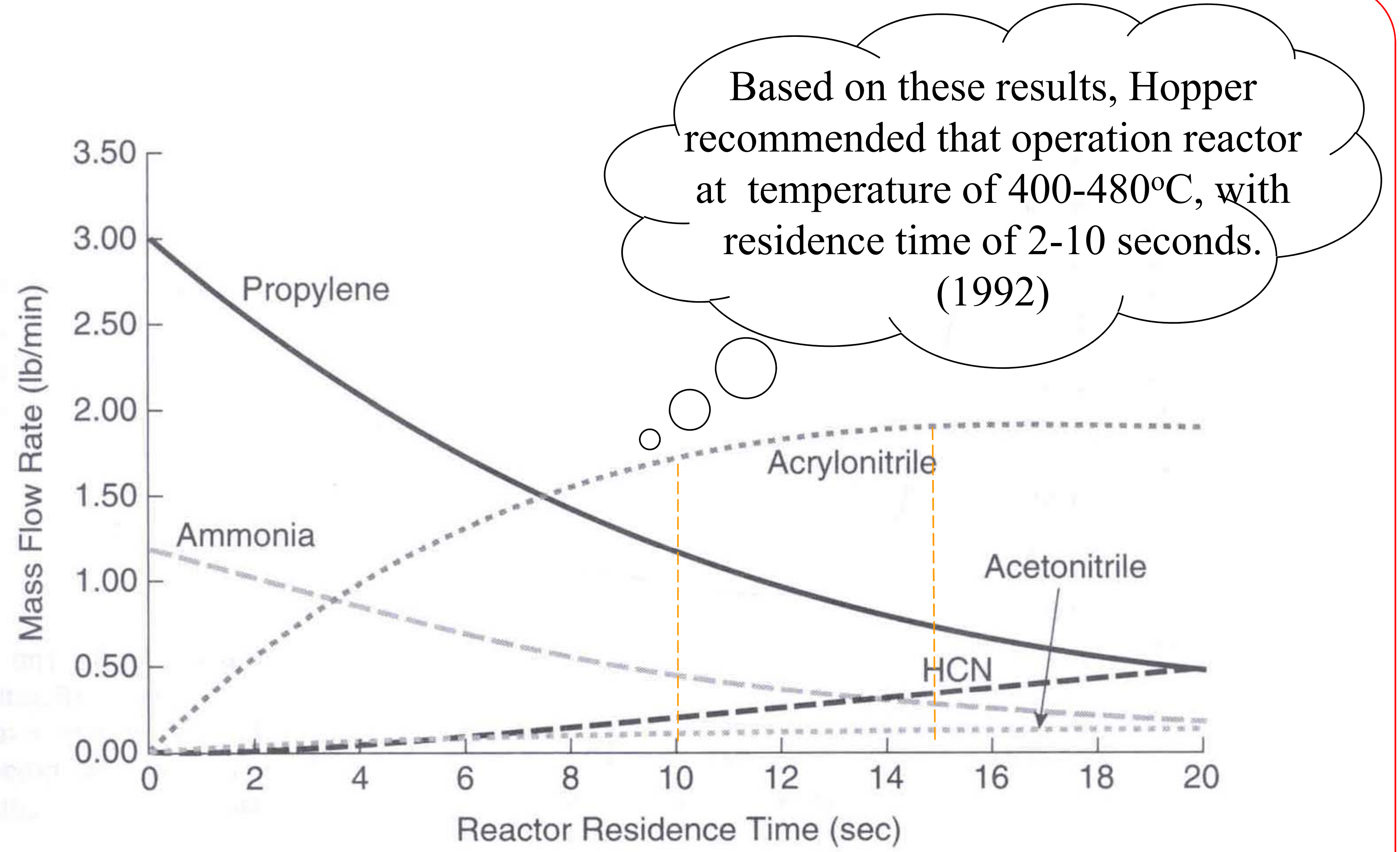
$CH_2{=}CH\text{-}CN + NH_3 + 2O_2 \rightarrow CO_2 + HCN + 3H_2O$

$CH_2{=}CN + 3/2O_2 \rightarrow CO_2 + CO + HCN + H_2O$

Case Study : Acrylonitrile

- Assumed reaction model : 1st order kinetics for reactant, product and byproduct species
- Model of Fluidized Bed Reactor was used to predict the effects of reaction temperature, and residence time on the generation of reaction byproducts in acrylonitrile reaction.
- FBR model predicts the optimum residence time for minimum waste generation and acceptable economic performance. The evaluation is based on both mass generation as well as risk generation approaches.

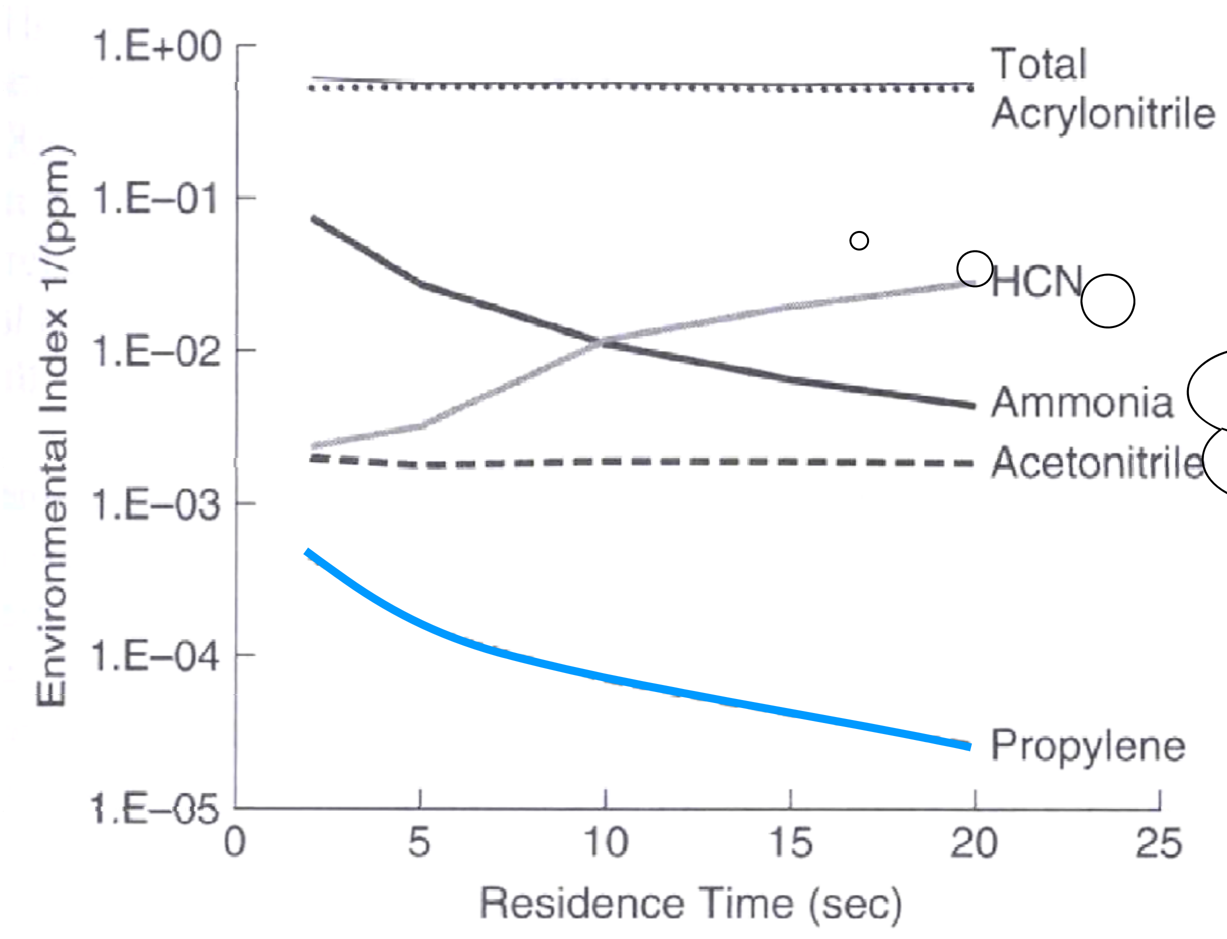
- ***Predicted Results for FBR Model***
  1. *Effect of residence time on concentration of propylene, ammonia, product, and byproduct* ***(Fig. 9.8-1)***
  2. *Effect of residence time on the conversion of propylene to products* ***(Fig. 9.8-2)***
  3. Total environmental index as a function of residence time to AN production via the ammonoxidation pathway ***(Fig. 9.8-3)***
  4. Raw material costs per mass of AN produced in ammonoxidation of propylene ***(Fig. 9.8-4)***



Based on these results, Hopper recommended that operation reactor at temperature of 400-480^{o}C, with residence time of 2-10 seconds. (1992)

Fig 9.8-1

Effect of reactor residence time on the conversion of propylene and ammonia to product(AN) and byproducts . The model is of a fluidized-bed reactor at 400 C. Byproduct generation is shown on a mass basis

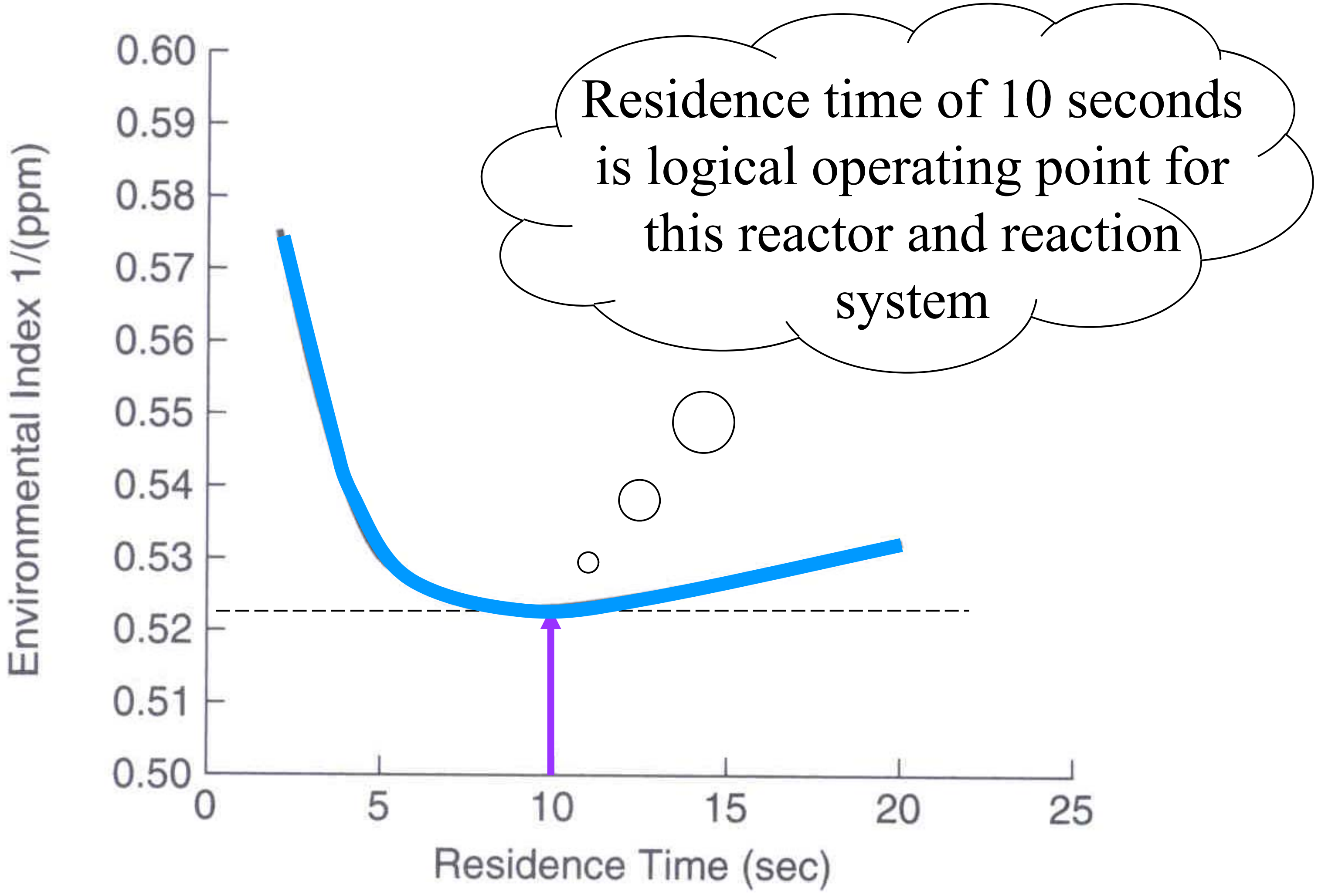


Using Fig. 9.8-1, Equation 8-2, and Table 8.2-11

Fig 9.8–2

Effect of reactor residence time on the conversion of propylene to product(A and byproducts . The model is of a fluidized-bed reactor at 400 C. Byproduct generation is shown on risk basis

Compound	Stoichiometry	1/TLV (ppm)-1	Cost per pound
Ammoxidation of Propylene			
Propylene	**-1.1**	**1/10,000**	**$0.13**
Ammonia	**-0.4**	**1/25**	**$0.07**
Acrylonitrile	**1**	**1/2**	**$0.53**
HCN	**0.1**	**1/10**	**$0.68**
Acetonitrile	**0.03**	**1/40**	**$0.65**



Residence time of 10 seconds is logical operating point for this reactor and reaction system

Fig 9.8-3

The total environmental index (eq. 8-2) as a function of reactor residence time for AN production via the ammonoxidation pathway

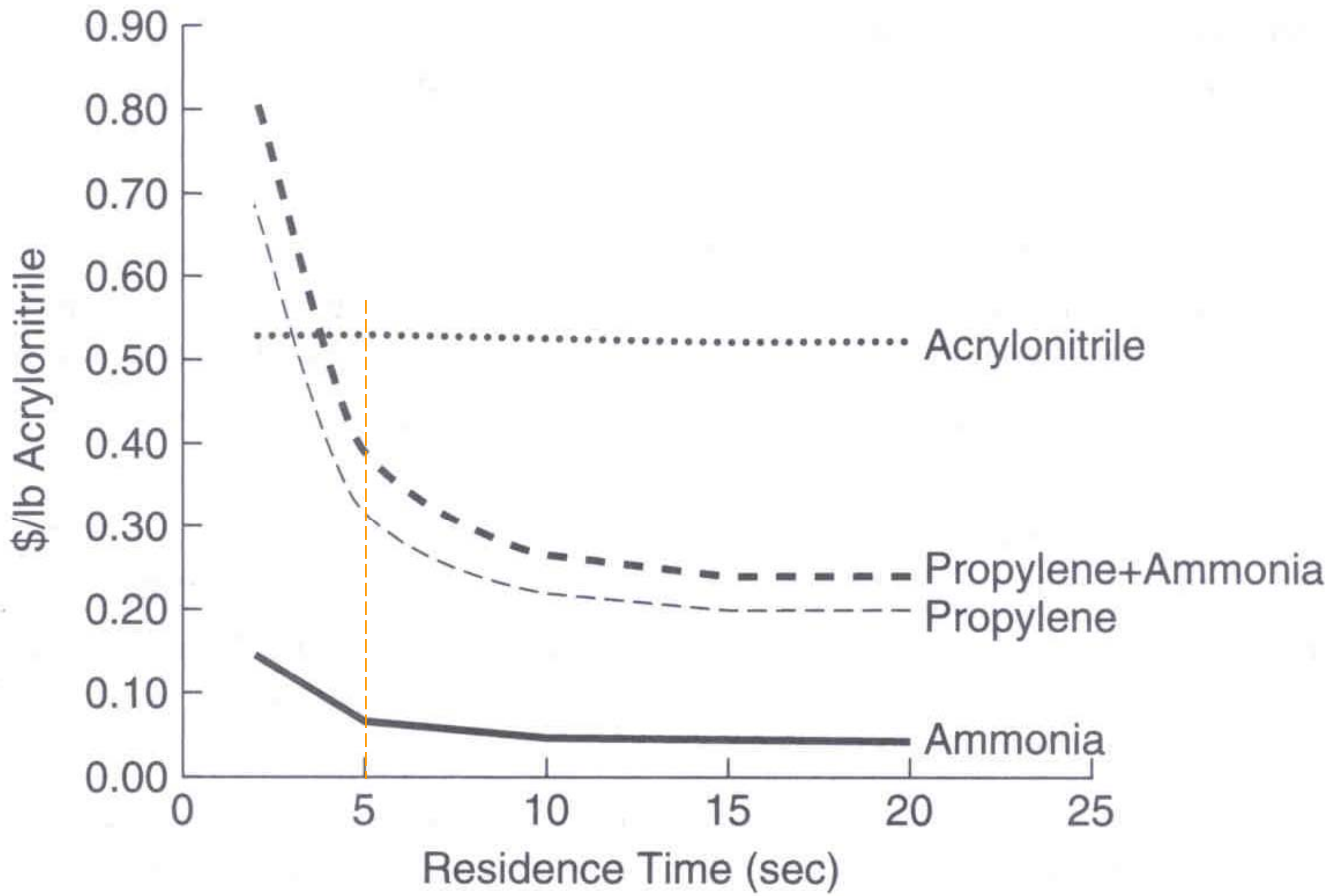


Fig 9.8-4

Raw materials costs per mass of acrylonitrile produced in a ammonoxiation of propylene

SUMMARY OF CASE STUDY

1. This case study demonstrates that “tier 1” environmental assessment from Chapter 8 combined with a screening economic analysis provides valuable insights into the overall performance of the reactor design (residence time).
2. There is little economic benefit in operating at residence times greater than 10 seconds, and the total environmental risk index is a maximum at 10 seconds. Therefore, a residence time of 10 seconds is a logical operating point for this reactor and reaction system.

Questions for Discussion

1. This chapter has considered pollution prevention alternatives for a variety of types of unit operations-reactors, separation devices, storage tanks and others. For a typical chemical process, which of these will be responsible for the majority of the emissions ? Does your answer depend on the type of pollutant or the environmental medium to which the pollutant is released

2. The pollution prevention alternatives identified here frequently result in reduced energy use and reduced material use. If the environmental improvements result in a design that uses less energy and less materials, why might a design engineer not choose to implement these options ?

Questions for Discussion

3. Pollution prevention alternatives have been considered for individual unit operations. Is it possible that a pollution prevention strategy implemented for one unit operation may increase wastes and emissions in another unit operation ? (Consider, the addition of emulsifiers in tanks to reduce solids formation. Can you think of other examples ?)