Environmental Evaluation and Improvement During Process Synthesis - Chapter 9 (b)

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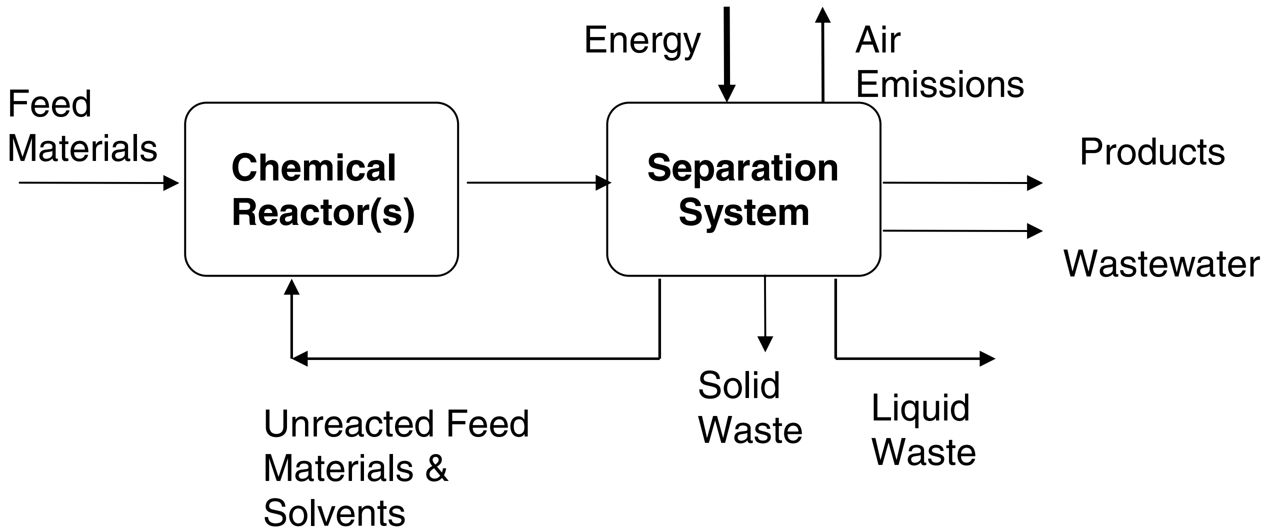
Chapter 9 (b): Outline

After the Input-Output structure is established, an environmental evaluation during process synthesis can identify large sources of waste generation and release; directing the attention of the designer to pollution prevention options within the process

- Educational goals and topics covered in the module
- Pollution prevention strategies for process units - ***Separations, Storage Tanks, Fugitive Sources, Separative Reactors, and Safety Concerns***

Chapter 9 (b): Separations - Potential problems / opportunities



Pollution Prevention Strategies

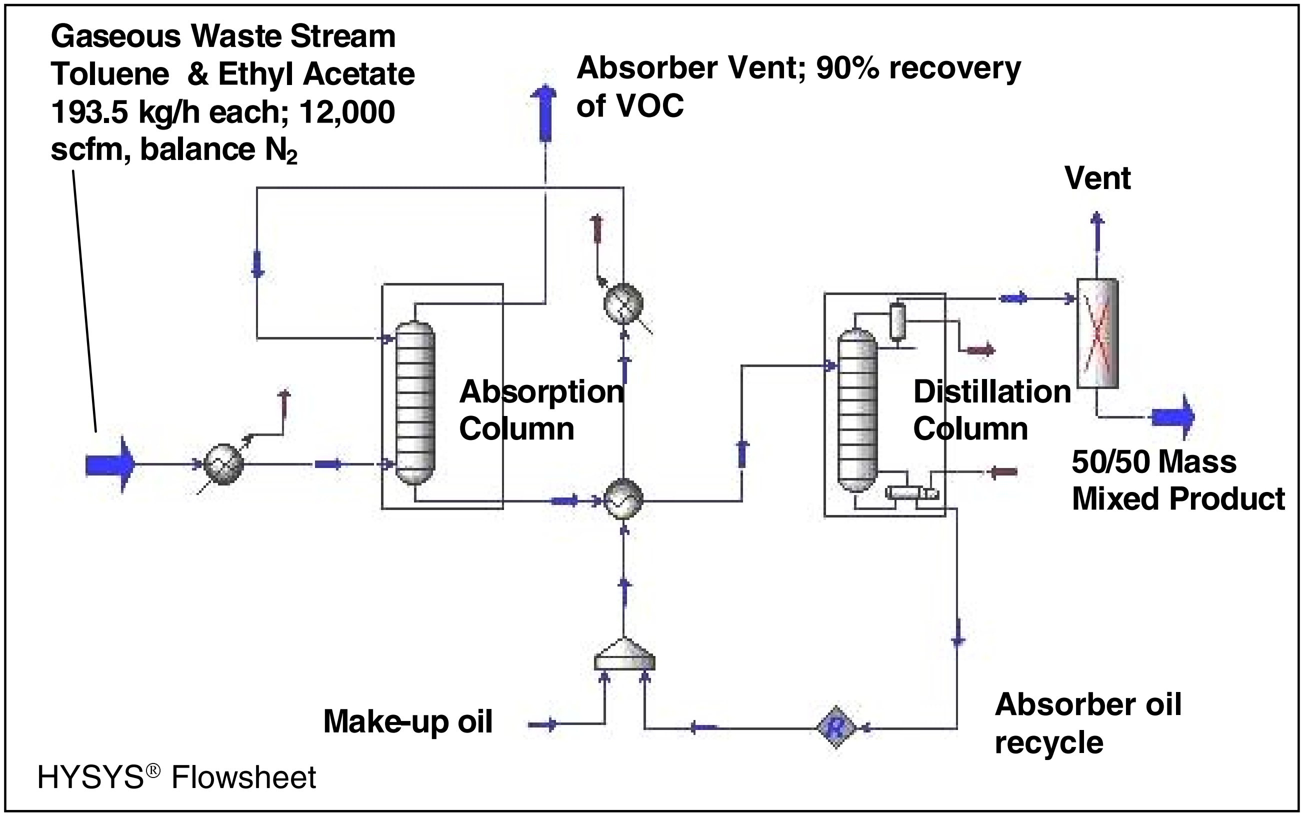
- Correct choice of separation technologies
- Choice of mass separating agents
- Design heuristics to prevent pollution
- Careful control of system parameters during operation

Chapter 9 (b): Separations - Choosing the best technology

Table 9.4-1 Unit operations for separations and property differences (Null, 1987).

Unit Operation	**Property Difference**
Adsorption	Surface Sorption
Chromatography	Depends Upon 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	Diffusivity and Solubility
Micro- and Ultrafiltration	Molecular Size

Chapter 9 (b): Pollution prevention - example of mass separating agent choice



MSA Screening

1. 857 chemicals
2. Hansen Sol. Par.
   - $11.8 < \delta_d < 22$
   - $0 < \delta_p < 9.3$
   - $0 < \delta_h < 11.2$
3. $T_{bp} > 220$ ˚C
4. $T_{mp} < 26$ ˚C
5. 23 chemicals remain

Conditions for simulations

1. 10-stage columns,
2. 10 ˚C approach temperature for heat integration,
3. absorber temperature = 32 ˚C

Chen, H., Barna, B.A., and Rogers, T.N., Shonnard, D.R., 2001, A screening methodology for improved solvent selection using economic and environmental Assessments, *Clean Products and Processes*, 3(3), 290-302.

Chapter 9 (b): Pollution prevention - results of mass separating agent choice

The difference in energy consumption is nearly a factor of 4.

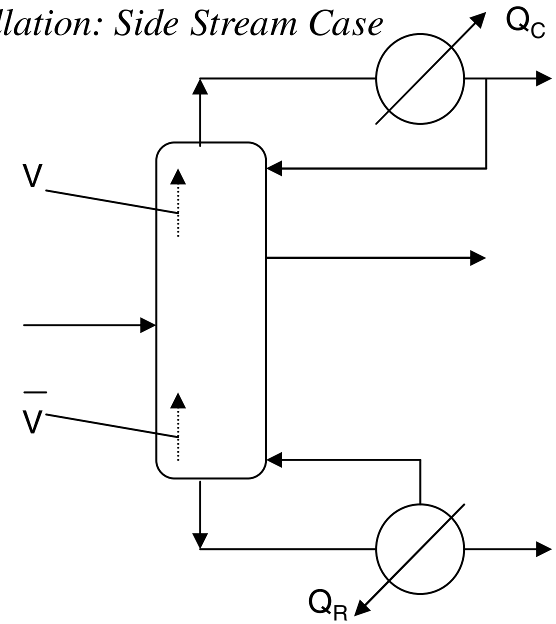
Chemical	*Utility (Btu/hr)*	*Rank*
o-Dibromobenzene	1.37×10^6	1
Butyl benzoate	1.39×10^6	2
Nitrobenzene	1.41×10^6	3
o-Bromoanisole	1.42×10^6	4
Dibenzyl ether	1.42×10^6	5
Diethylene glycol dibutyl ether	1.46×10^6	6
Diethylene glycol butyl ether acetate	1.46×10^6	7
Octanioc acid	1.47×10^6	8
Ethyl cinnamate	1.48×10^6	9
1-Bromo-4-ethoxy benzene	1.49×10^6	10
trans-Anethole	1.62×10^6	11
Diethylene glycol monobutyl ether	1.68×10^6	12
1-Methyl naphthalene	1.70×10^6	13
p-Chlorobenzoyl chloride	1.75×10^6	14
4-Chlorobenzotrichloride	1.75×10^6	15
Diethylene glycol monoethyl ether acetate	1.83×10^6	16
Quinoline	2.30×10^6	17
1-Decanol	2.37×10^6	18
2-Decanol	2.55×10^6	19
Hexadecane	3.39×10^6	20
Tetradecane	3.94×10^6	21
1,2,4-Trichlorobenzene	3.95×10^6	22
Dodecane	5.35×10^6	23

Chapter 9 (b): Separations - Common sense solution to distillation

Example Problem 9.4-1

Energy Savings in Distillation: Side Stream Case

Feed
F = 100 moles/hr
x_F = 0.4 mole fraction
(1/2 vapor, 1/2 liquid)



Distillate
D
$X_D = 0.8$

Side Stream
S = 20 moles/hr
$X_S = 0.65$

Bottoms
B
$X_D = 0.02$

Energy Savings Of about 30%

Solution:

Column Design	***L/D***	***D***	$\bar{V}$	Q_R (cal/hr)
Side Stream	2.5	32.56	63.96	$63.96\text{x}10^4$
No Side Stream	2.0	48.72	96.16	$96.16\text{x}10^4$

Chapter 9 (b): Separations - Design heuristics (guidance) for pollution prevention

Table 9.4-2 Separation Heuristics to Prevent Pollution (Adapted from Mulholland 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

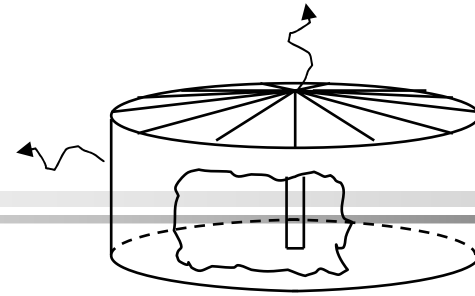
Separations - pollution prevention examples

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, reduce incineration loads by 4 million lb/yr, and had a payback period of only 2 years.	(Mulholland and Dyer, 1999)
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.)
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)
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)
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, recovery of vinyl chloride from PVC reactor vents, and recovery of chlorofluorocarbons (CFCs) 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)

Allen, D.T. and Shonnard, D.R., "Green Engineering: Environmentally Conscious Design of Chemical Processes, Prentice-Hall, Upper Saddle River, NJ, 2002

Storage Tank Emissions: Solvent Mass Calculation



- Calculate net emissions reduction for application of new paint to existing fixed roof tank
  - → Old dark paint in poor condition: **509.7** lb/yr emitted
  - → New white paint: **337.6** lb/yr

    50% (vol) solvent in paint, 100 sq. ft./gal of paint, solvent density = 6 lb/gal

Dark Paint: Basis 10 years

Total VOC Emission = (10 yr) (509.7 lb/yr) = **5,097 lb**

New White Paint: Basis 10 years

Surface Area of a 16 ft dia and 10 ft tall Tank = 703.7 ft^2

$$\text{Total Solvent Emission} = (10\text{ yr})(337.6\text{ lb/yr}) + \frac{(703.7\text{ ft}^2)(6\text{ lb/gal})}{(100\text{ ft}^2/\text{gal})} = \mathbf{3{,}418.2\text{ lb}}$$

Chapter 9 (b): Fugitive Sources - pollution prevention techniques

Table 9.6-4 Effectiveness of Various Fugitive Emission Reduction Techniques

		Control Effectiveness (%)	
Equipment	**Control Technique**	**SOCMI**	**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

Allen, D.T. and Shonnard, D.R., “Green Engineering: Environmentally Conscious Design of Chemical Processes, Prentice-Hall, Upper Saddle River, NJ, 2002

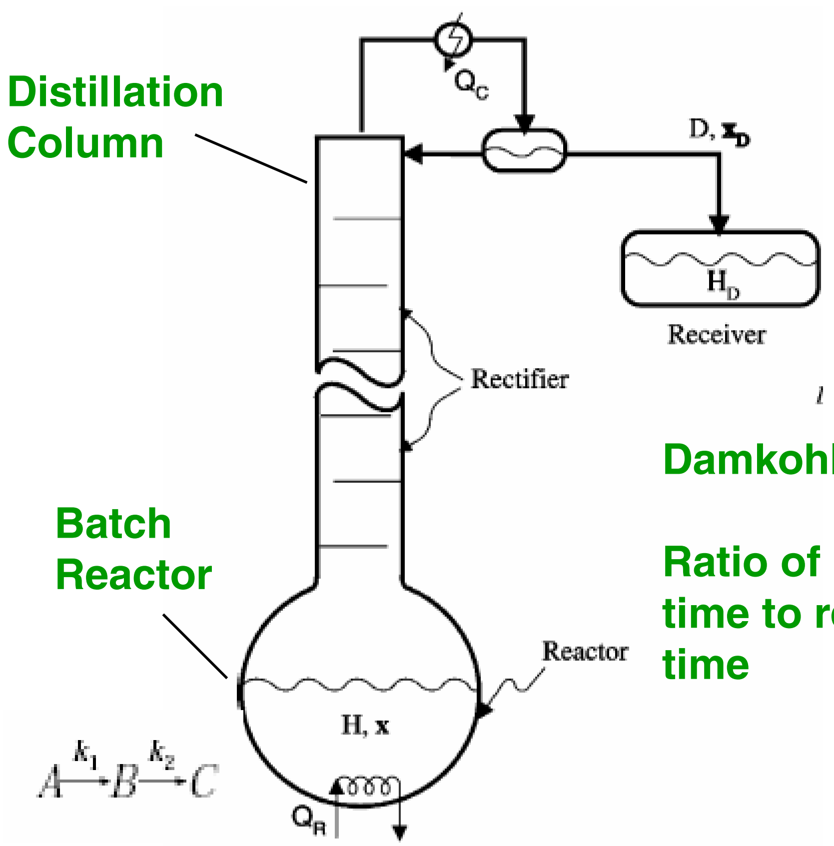
Chapter 9 (b): Separative reactors - key features

- Combine chemical reaction with separation in a single unit
- Reduce waste generation
  - » Shift chemical equilibrium to favor product formation by removing products from reaction mixture
  - » Remove desired product in series reactions thereby reducing waste generation via secondary reactions
- Maximize product yields
- Separation technologies used
  - » Distillation
  - » Adsorption
  - » Membranes

Chapter 9 (b): Batch Reactive Distillation (BRD)

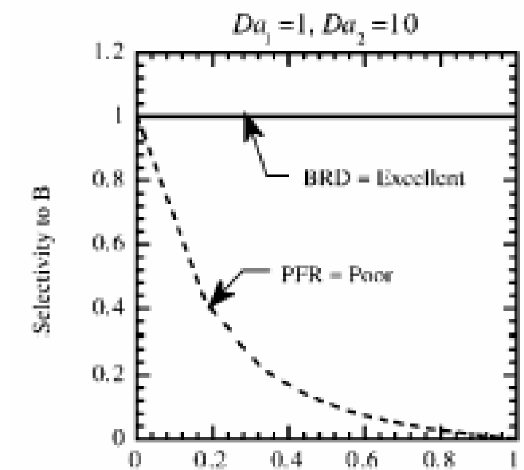
Distillation Column

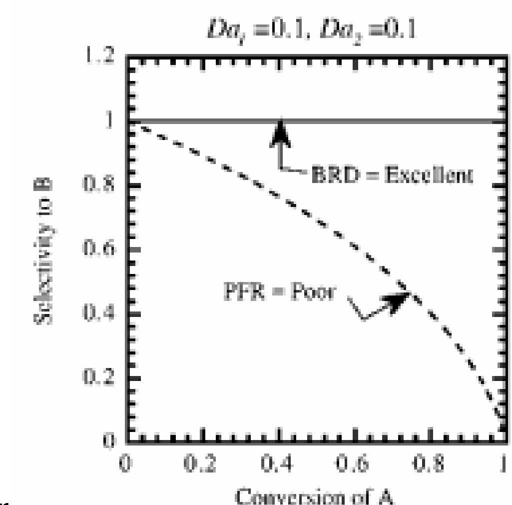
Batch Reactor



Damkohler No., *Da*

Ratio of process time to reaction time



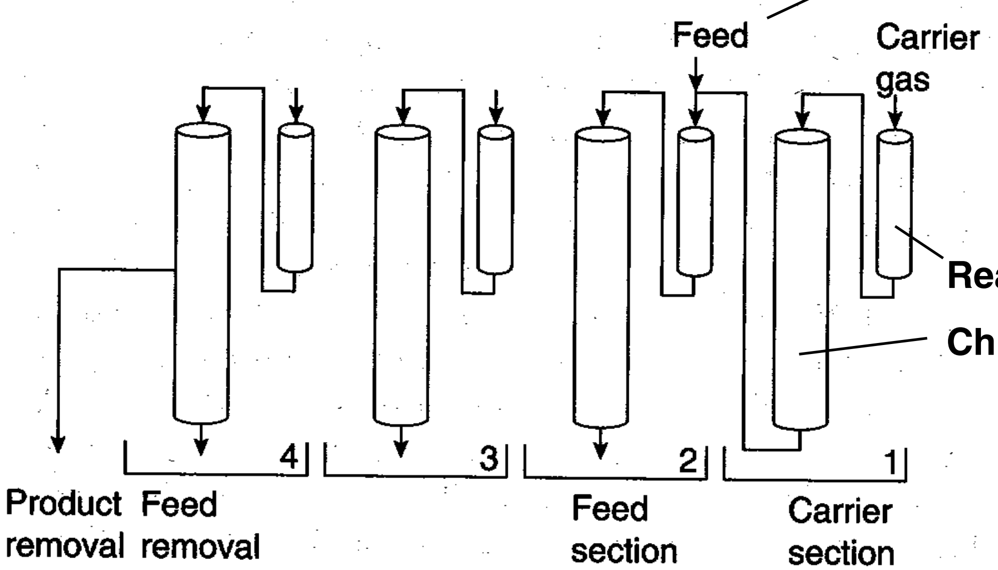


Malone, M.F., Huss, R.S., and Doherty, M.f., "Green Chemical Engineering: Aspects of Reactive Distillation, 2003, ES&T, 37(23), 5325-5329.

Chapter 9 (b): Separative reactors - with adsorption

Simulated Countercurrent Moving-bed Chromatographic Reactor

CH_4 + O_4 in stoichiometric amts



Reactors (1,000 ºK)

Chromatographic Columns (cool)

Desired Reactions

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + H_2O$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$$

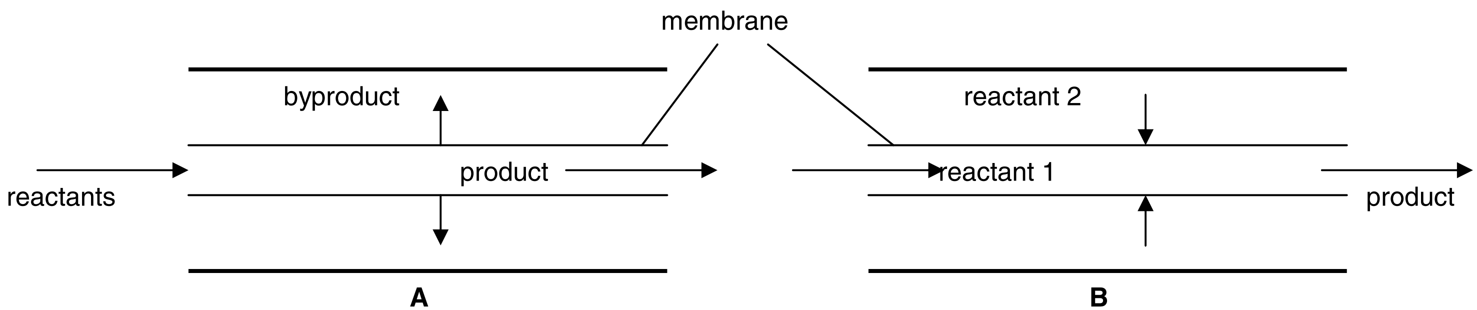
Waste Reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Yields of product from CH_4 increase from <20% to > 50%

Allen, D.T. and Shonnard, D.R., "Green Engineering: Environmentally Conscious Design of Chemical Processes, Prentice-Hall, Upper Saddle River, NJ, 2002

Chapter 9 (b): Separative reactors - with membranes



Product/byproduct removal mode

Reactant addition mode of operation

$$CH_3CH_2 - C_6H_6 \rightarrow CH_2CH - C_6H_6 + H_2$$

Dehydrogenation of ethylbenzene to styrene reaction

Yields of product increase 15% and selectivity increases 2-5%

Chapter 9 (b):
Safety concerns with pollution prevention

- Pollution prevention applications may make a chemical process more complex, thereby increasing safety concerns.

Example problem 9.7-1
Safety concerns for storage tank pollution prevention

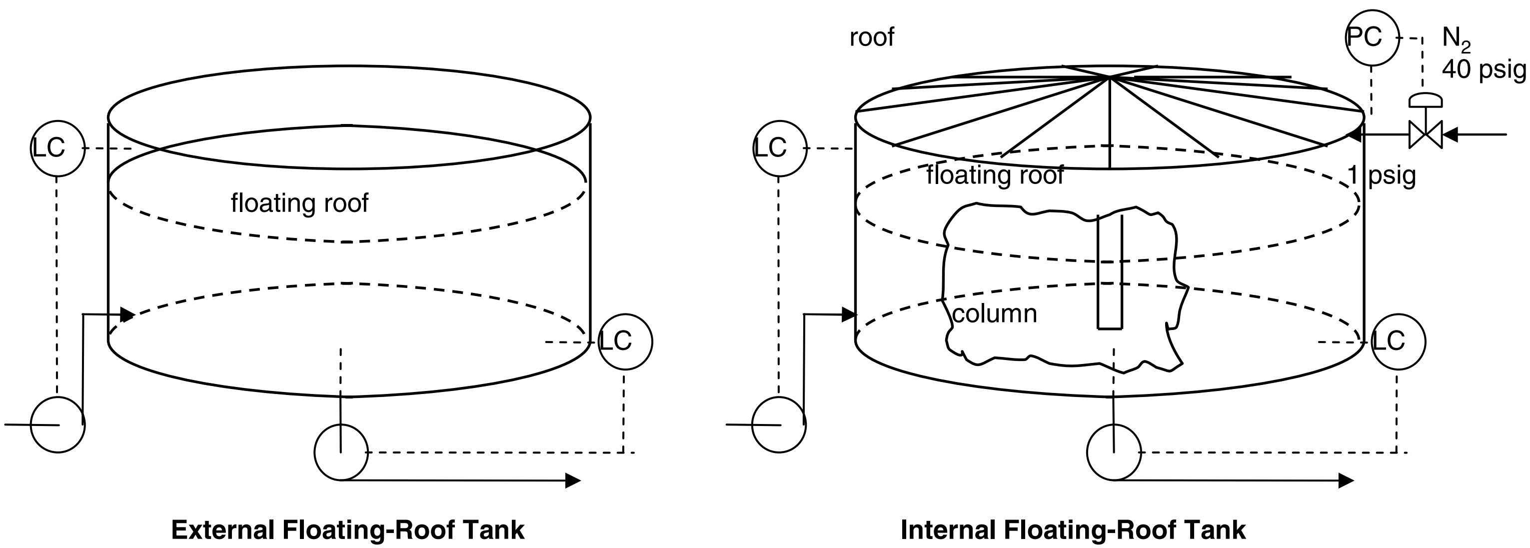


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Table 9.7-2 Limited HAZ-OP Analysis of storage tank pollution prevention

Guide Words	Deviation	EFRT	IFRT	Possible Cause	Consequences
NO	Inlet pump fails to stop or Outlet pump fails to start	X	X	1. Level gauge fails 2. Pump fails	1. Toluene spills out top of tank 2. Soil and ground water contamination 3. Exposure to site personnel
MORE	Inert N_2 fails to stop		X	1. Pressure control fails	1. Overpressure of storage tank and tank roof failure 2. Tank rupture and spill of toluene
LESS	Inert N_2 insufficient		X	1. N_2 supply interruption	1. flammable mixture of Toluena + air
AS WELL AS	Water in tank	X	X	1. Floating roof leak in EFRT 2. External roof lead in IFRT	1. Contamination of toluene product and generation of additional waste
PART OF	Inert N_2 insufficient		X	1. Covered under LESS	1. Covered under LESS
REVERSE	Pumps reverse	X	X	1. Impossible	1. Level control failure and spill of toluene
OTHER THAN	Another inerting gas		X	1. Another gas is used	1. If O_2 is used by mistake, a flammable mixture is created.

EFRT – External Floating-Roof Tank
IFRT – Internal Floating-Roof Tank

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Chapter 9 (b): Summary/Conclusions

Many opportunities to reduce waste generation within unit operations

- Separation units
- Material choices can affect energy consumption
- Storage tanks - some types are inherently less polluting
- Fugitive sources - some types of equipment emit less VOCs
- Separative reactors can increase reaction yield and selectivity
- Safety concerns originate from the increase in complexity of pollution prevention design modifications