# Preventing Pollution:
# Choices During Process Synthesis - Chapter 9

David R. Shonnard
Department of Chemical Engineering
Michigan Technological University



## Chapter 9 (a): 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 - ***Material selection and chemical reactors***
- Pollution prevention strategies for process units - ***Separations, Storage Tanks, Fugitive Sources, Separative Reactors, and Safety Concerns***

## Educational goals and topics covered in Chapter 9

### Students will:

1 become familiar with practical pollution prevention strategies for process units



## Chapter 9: Important issues regarding pollution prevention for unit operations

1. *Material selection*: fuel type, mass separating agents (MSAs), air, water, diluents, heat transfer fluids
2. *Operating conditions*: temperature, pressure, mixing intensity
3. *Energy consumption*: high efficiency boilers, operation of units to minimize energy usage
4. *Material storage and fugitive sources*: storage tank choices and equipment monitoring and maintenance
5. *Waste generation mechanisms*: understanding this will lead to pollution prevention strategies

# Chapter 9: Pollution prevention through material selection - fuel type

*Example Problem:*

*Calculate the annual uncontrolled $SO_2$ emissions to satisfy a steam energy demand of $10^8$ Btulyr with a boiler efficiency of .85 assuming Fuel Oil #6, #2, and Natural Gas.*

| | **#6 Fuel Oil** | **#2 Fuel Oil** | **Natural Gas** |
|---|---|---|---|
| Emission Factor, ***EF*** (lb/$10^3$ gal) | 157S | 143S | 0.6 lb/$10^6$ scf |
| Sulfur Content, ***S*** % | 0.84 | 0.24 | ---- |
| Heating Value, ***HV*** (Btu/$10^3$ gal) | 1.48x$10^8$ | 1.30x$10^8$ | 1050x$10^6$ Btu/$10^6$scf |
| Annual Emission, ***E*** (lb $SO_2$/yr) | **105** | **31** | **.07** |

$$E_i(\text{lb } i/\text{yr}) = \frac{EF_{av}(\text{lb } i/10^3\text{gal}) \times ED(\text{Btu/yr})}{HV(\text{Btu}/10^3\text{ gal}) \times BE}$$

$$E_i(\text{lb } i/\text{yr}) = \frac{EF(\text{lb } i/10^6\text{scf}) \times ED(\text{Btu/yr})}{HV(\text{Btu}/10^6\text{scf}) \times BE}$$



# Chapter 9: Pollution prevention through material selection - reactor applications

1. *Catalysts*:
   - that allow the use of more environmentally benign raw materials - e.g. ***less hazardous raw materials***
   - that convert ***wastes to usable products and feedstocks***
   - products more environmentally friendly - e.g. RFG / low S diesel fuel
2. *Oxidants*: in partial oxidation reactions
   - ***replace air with pure $O_2$*** or enriched air to reduce NOx emissions
3. *Solvents and diluents* :
   - ***replace toxic solvents*** with benign alternatives for polymer synthesis
   - ***replace air with $CO_2$*** as heat sinks in exothermic gas phase reactions

# Chapter 9: Pollution prevention for chemical reactors

1. *Reaction type*:
   - series versus parallel pathways
   - irreversible versus reversible
   - competitive-consecutive reaction pathway

2. *Reactor type*:
   - issues of residence time, mixing, heat transfer

3. *Reaction conditions*:
   - effect of mixing on yield and selectivity

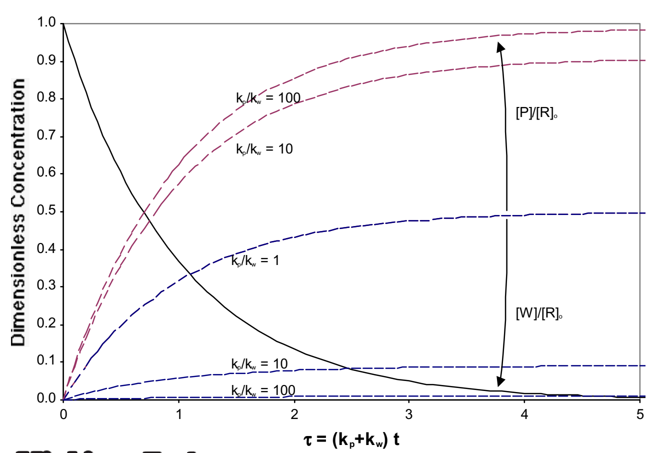


# Chapter 9: Pollution prevention for chemical reactions

***1st Order Irreversible Parallel Reactions***

$$R \xrightarrow{k_p} P$$

$$R \xrightarrow{k_w} W$$




**High Conversion**
$t > 5(k_p + k_w)^{-1}$

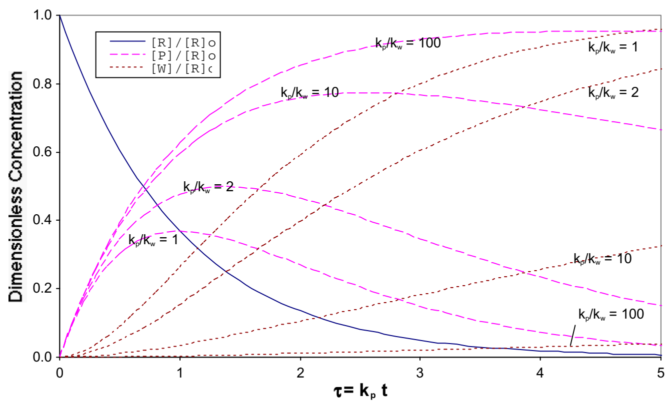
**High Selectivity**
$k_p >> k_w$

**Selectivity Independent of residence time**

# Chapter 9: Pollution prevention for chemical reactions

***1st Order Irreversible Series Reactions***

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




**High Conversion**
$t > 5\ k_p^{-1}$

**High Selectivity**
$k_p >> k_w$

**Selectivity dependent on residence time**



# Pollution prevention for chemical reactions

***Reversible Series Reactions***

Steam reforming of $CH_4$

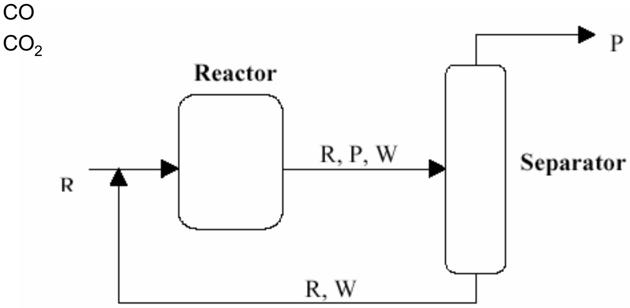
$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$

R = $CH_4$

P = CO

W = $CO_2$



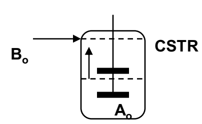

*Separate and recycle waste to extinction*

# Chapter 9:
# Pollution prevention - reactor types

1. *CSTR*:
   - not always the best choice if residence time is critical
2. *Plug flow reactor*:
   - better control over residence time
   - temperature control may be a problem for highly exothermic reactions
3. *Fluidized bed reactor* :
   - if selectivity is affected by temperature, tighter control is possible
4. *Separative reactors*:
   - remove product before byproduct formation can occur: series reactions



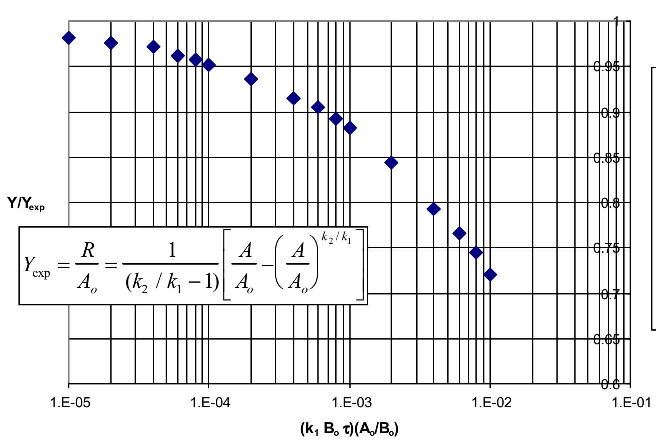
# Chapter 9:
# Pollution prevention - mixing effects




***Irreversible 2nd order competitive-consecutive reactions***

$$A + B \xrightarrow{k_1} P$$

$$P + B \xrightarrow{k_2} W$$




$$Y_{\exp} = \frac{R}{A_o} = \frac{1}{(k_2/k_1 - 1)}\left[\frac{A}{A_o} - \left(\frac{A}{A_o}\right)^{k_2/k_1}\right]$$

Y = yield
= $P/A_o$
$Y_{exp}$ = expected yield
$\tau$ = mixing time scale

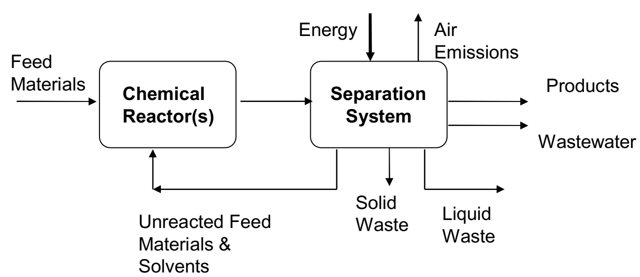
***Increased mixing will increase observed yield***

## Chapter 9 (a): Pollution prevention - other reactor modifications

1. *Improve Reactant Addition*:
   - premix reactants and catalysts prior to reactor addition
   - add low density materials at reactor bottom to ensure effective mixing
2. *Catalysts*:
   - use a heterogeneous catalyst to avoid heavy metal waste streams
   - select catalysts with higher selectivity and physical characteristics (size, porosity, shape, etc.)
3. *Distribute flow in fixed-bed reactors*
4. *Heating/Cooling*:
   - use co-current coolant flow for better temperature control
   - use inert diluents ($CO_2$) to control temperature in gas phase reactions
5. *Improve reactor monitoring and control*



## Chapter 9: Separations - Potential problems / opportunities

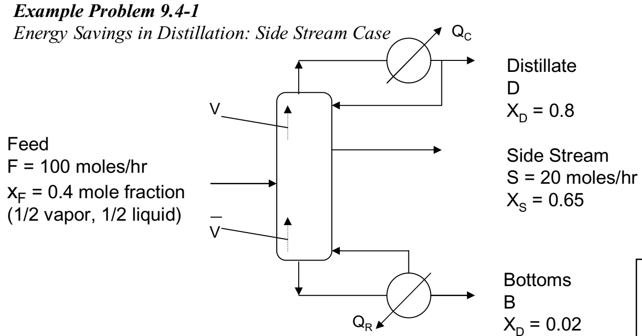



### *Pollution Prevention Strategies*

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

# Chapter 9: Separations - Common sense solution to distillation

***Example Problem 9.4-1***
*Energy Savings in Distillation: Side Stream Case*



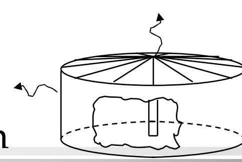

**Energy Savings Of about 30%**

*Solution*:

| **Column Design** | ***L/D*** | ***D*** | $\bar{V}$ | $Q_R$ (cal/hr) |
|---|---|---|---|---|
| Side Stream | 2.5 | 32.56 | 63.96 | 63.96x10$^4$ |
| No Side Stream | 2.0 | 48.72 | 96.16 | 96.16x10$^4$ |



# Storage Tank Emissions: Solvent Mass Calculation



1 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$^2$

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

## Chapter 9: 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<br>Monthly leak detection and repair<br>Quarterly leak detection and repair | 100<br>60<br>30 | 100<br>80<br>70 |
| Valves, gas/light liquid service | Monthly leak detection and repair<br>Quarterly leak detection and repair | 60<br>50 | 70<br>60 |
| Pressure-relief devices | Tie to flare; rupture disk<br>Monthly leak detection and repair<br>Quarterly leak detection and repair | 100<br>50<br>40 | 100<br>50<br>40 |
| Open-ended lines | Caps, plugs, blinds | 100 | 100 |
| Compressors | Mechanical seals;<br>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



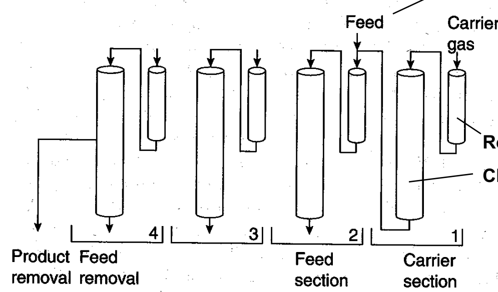
## Chapter 9: Separative reactors – key features

- 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: Separative reactors - with adsorption

Simulated Countercurrent Moving-bed Chromatographic Reactor

**$CH_4$ + $O_4$ in stoichiometric amts**




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

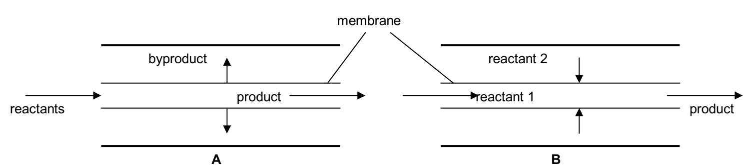
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

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: Separative reactors - with membranes




Product/byproduct removal mode

Reactant addition mode of operation

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

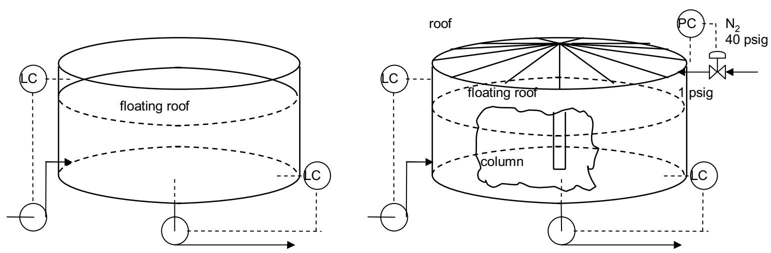
Dehydrogenation of ethylbenzene to styrene reaction

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

# Chapter 9: 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*




**External Floating-Roof Tank** **Internal Floating-Roof Tank**

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



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

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

# Chapter 9: Summary/Conclusions

1. ***Pollution prevention for chemical reactions and reactors***:
    - material choices for reactions
    - reactor types (CSTR, plug flow, fluid bed, etc.)
    - reaction conditions (temperature, mixing, concentration effects)

***2. Pollution prevention for within other 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