Pollution Prevention and Risk Reduction for Chemical Processes

Module 4:
Improving the Environmental Performance of Unit Operations and Flowsheets

Background Reading:
D. R. Shonnard, Chapter 9 "Unit Operations and Pollution Prevention"

By the end of the completed section you should:

- **be familiar with waste generation and pollutant release mechanisms for specific unit operations within chemical processes**
- **be able to identify pollution prevention opportunities for specific unit operations**
- **be able to perform screening level risk evaluation of input and output streams from specific unit operations**

Outline:

I. Detailed outline of Chapter 9
II. Storage tank pollution prevention
  A. Vent emission reduction strategies
III. Reactor pollution prevention
  A. Reactor operation and it's effects on waste generation

I. Detailed Outline of Chapter 9

9.1 INTRODUCTION
Purpose of the chapter and brief discussion of each section.

9.2 POLLUTION PREVENTION IN MATERIAL SELECTION
What are the important properties of materials when considering pollution prevention and environmental risk reduction? Example applications of PMN tool. How are material selection and unit operations connected?

9.3 POLLUTION PREVENTION FOR CHEMICAL REACTORS
A. Material Use and Selection (most general topic)
    1. Solvent Selection.
    2. Catalyst Issues -----> Example Problem
    3. Raw Material Issues
B. Reactions and Reactors (Intermediate level of detail)
    1. Equilibrium Reactions - Recycle byproducts ---> Example Problem
    2. Sequential Reactions - Remove products
    3. Temperature / Heating / Cooling Issues
C. Types of Reactors
    1. Fluidized versus Packed Bed.
D. Reactor Operation (most specific)
    1. Mixing Issues, Example Problem
    2. Reactant Addition
    3. Control of Critical Parameters - Calibration of Instrumentation.
E. References: (11, 3, 8, 12, 10, 5, 6, 15, 2, 1, 9, 7)

9.4 POLLUTION PREVENTION FOR SEPARATION DEVICES
A. Reducing routine wastes (control excursions, increase efficiency)
B. Technology applications for in process pollution prevention
    1. Distillation applications
    2. Absorption applications
    3. Adsorption applications
    4. Membrane applications
References: (13, 1, 14)

9.5 POLLUTION PREVENTION APPLICATIONS FOR SEPARATIVE REACTORS
Applications of separative reactors for pollution prevention
References: (14)

9.6 POLLUTION PREVENTION IN STORAGE TANKS AND FUGITIVE SOURCES
a) Choices in technology selection and maintenance programs.
References: (3)

9.7 POLLUTION PREVENTION ASSESSMENT INTEGRATED WITH HAZ-OP ANALYSIS (Imbed in Each Unit Operation)
HAZOP Analysis is a dynamic analysis of a steady state flow sheet. What do dynamic perturbations do to emissions and waste generation?
    1. Overview of HAZ-OP analysis.
    2. Description of potential tradeoffs between environmental risk reduction and

process safety.
References: (4)

9.8 INTEGRATING RISK ASSESSMENT WITH PROCESS DESIGN
How do we start to evaluate process flowsheets for their environmental and human health impacts? Which tools and methodologies are currently available and/or in the developmental stages?
References:
Several journal articles and EPA documents. Focus on PMN process.

9.9 CASE STUDIES
Storage Tank Selection
Reactor optimization for waste reduction (acrylonitrile reactor study)

Outline References

1. Abasi-Halabi, M. et al, Trends in catalysis researach to meet future refining needs, Hydrocarbon Processing, Feb. 1997, p45 - 55

2. Arakawa, S.T. et al., Increase productivity with novel reactor design, Hydrocarbon Processing, March 1998, p 93 - 100.

3. Allen, D.T. and Rosselot, K., Pollution Prevention for Chemical Processes, Wiley, 1997, ch6.

4. Crowl, D.A. and Louvar, J., Fundamentals of Process Safety, Prentice Hall, 1992.

5. DeSimone, J.M. et al., synthesis of fluoropolymers in supercritical carbon dioxide, Science, Fol. 257, 14 Aug. 1992, p. 945 - 947.

6. DeSimone, J.M. et al., Dispersion polymerizations in supercritical carbon dioxide, Science, Vol. 265,15 July, 1994, p. 356 - 359

7. Elias, H-G., Macromolecules, Volume 2 Synthesis, Materials, and Technology, Plenum Press, New York, 1984.

8. Hopper, J.R., Pollution prevention through reactor design, in Industrial Pollution Prevention Handbook, ed Freeman, H.M., McGraw-Hill, 1995, ch 22.

9. Komiya, K. et al., New process for producing polycarbonate without phoshene and methylene chloride, in Green Chemistry: Designing Chemistry for the Environment, ED P.T. Anastas and T.C. Williamson, ACS Symposium Series 626, American Chemical Society, Washington, DC, 1996, p 20-32.

10. Morgenstern et al. Supercritical carbon dioxide as a substitute solvent for chemical synthesis and catalysis, in Green Chemistry: Designing Chemistry for the Environment, ED P.T. Anastas and T.C. Williamson, ACS Symposium Series 626, American Chemical Society, Washington, DC, 1996, p 132-151.

11. Mulholland, K.L. and Dyer, J.A., Pollution Prevention: Methodology, Technologies and Practices, AIChE, 1999, ch10 p 131 _ 138.

12. Munzio, F.J. and Paul, E.L., Mixing as a tool for pollution prevention in reactive systems, in Industrial Pollution Prevention Handbook, ed Freeman, H.M., McGraw-Hill, 1995, ch 27.

13. Palepu, P.T., chauhan, S.P. and Ananth, K.P.., Separation technologies, in Industrial Pollution Prevention Handbook, ed Freeman, H.M., McGraw-Hill, 1995, ch 23

14. Radecki, P. , J.C. Crittenden, D.R. Shonnard, and J. Bullock, 1999, "Emerging Separation and Separative-Reactor Technologies for Process Waste Reduction: Adsorption and Membrane Systems", Center for Waste Reduction Technologies, American Institute of Chemical Engineers, New York, NY.

15. Sullivan, D.A., Solvents - Industrial, in Encyclopedia of Chemical Technology, Vol. 22, Kroschwitz, J.I. Executive Editor, John Wiley and Sons, p. 529 - 571, 1996.

II. Storage Tank Pollution Prevention

Storage tanks are very common unit operations in several industrial sectors, including petroleum production and refining, petrochemical and chemical manufacturing, storage and transportation, and other industries that either use or produce organic liquid chemicals. Tanks are used for many purposes, including storage of fuels and for buffer capacity for feedstocks and final products. The main environmental impact of storage tanks are the continual occurrence of air emissions of volatile organic compounds from roof vents and the periodic removal of oily sludges from tank bottoms.

Tank bottoms are solids or sludges composed of rusts, soil particles, heavy feedstock constituents, and other dense materials that are likely to settle out of the liquid being stored. There are various methods of dealing with these materials once they are present. They may be periodically removed and either treated via land application or disposed of as hazardous waste. As long as the bottoms components are compatible with downstream processes, they may be prevented from settling to the tank bottom by the action of mixers that keep the solid particles suspended in the liquid (API, 1991a). Another method is to use emulsifying agents that keep water and solids in solution and out of the tank bottoms. A concern with the use of this method is the potential to generate oily waste downstream in the refinery processes from the presence of the emusifiers (API, 1991b).

Air emissions of volatile organic compounds from storage tanks are a major source of airborne pollution from petroleum and chemical processing facilities. These emissions stem from the normal operation of these units in response to the changes in liquid level within the tank and the action of ambient changes in temperature and pressure. These loss mechanisms are termed *working losses* and *standing losses*, respectively. The emissions are dependent upon the vapor pressure of the stored liquids, tank characteristics such as tank type, paint color and condition, and also the geographic location of the tank. There are six major types of storage tanks. A listing of these types, a short description, a summary of emission mechanisms, and pollution reduction measures are listed in Table 9.6-1.

Table 9.6-1 Storage Tank Types and Pollution Reduction Strategies

Storage Tank Type	**Description**	**Loss Mechanisms**	**Pollution Reduction**
Fixed Roof (vertical {large}and horizontal {<40,000 gallons})	Vertical - cylindrical shell with permanent roof (flat, cone, or dome), freely vented or with pressure / vacuum vent.	Working losses – VOCs in headspace above liquid expelled when tank is filled. Standing losses – headspace gas expands / contracts by ambient ΔT and ΔP.	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.
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 a 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. 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.
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.

Vapor balancing involves routing the expelled vapors during tank filling to another tank that is supplying the liquid.
ΔT are daily changes in ambient temperature
ΔP are changes in barometric pressure

The following example problem will illustrate the emission reduction that is possible when substituting an internal floating roof tank or a domed external floating roof tank for a fixed roof tank in a process design.

Example problem 9-1

A toluene product stream, having a net throughput of 516,600 gal/yr, is to be recovered from a gaseous waste stream at a facility in the vicinity of Detroit, MI. Using the TANKS4.0 software (US EPA TTN, 1999), calculate and compare the uncontrolled annual emissions for a new tank design having the following dimensions and conditions;

Fixed Roof Tank: Height = 20 ft,Diameter = 12 ft, Working Volume = 15,228.53 gallons, Maximum Liquid Level = 18 ft, Average Liquid Level = 10 ft, no heating, domed roof of height 2 ft and diameter of 12 ft, vacuum setting of -.03 psig and pressure setting of .03 psig

Internal Floating Roof Tank: Height = 20 ft, Working Volume = 15,228.53 gallons, self supporting roof, internal shell condition of light rust, primary seal is a mechanical shoe, secondary shoe is shoe mounted, deck type is welded, deck fitting category is typical.

Domed External Floating Roof Tank: same as Internal Floating Roof Tank.

Solution

The TANKS4.0 program allows the user to quickly calculate the annual emission rate for all three tank types. The results are

Fixed Roof Tank: 337.6 lb/yr
Internal Floating Roof Tank: 66.2 lb/yr.
Domed External Floating Roof Tank: 42.8 lb/yr.

Discussion: The reduction in emissions for the floating roof tanks are:
Internal Floating Roof Tank: % reduction = (337.6-66.2)/337.6 x 100 = 80.4%
Domed External Floating Roof Tank: % reduction = (337.6-42.8)/337.6 x 100 = 87.3%

The reductions are significant, and may help the facility achieve emission reduction targets established by local, state, and federal regulations. Floating roof tanks are more expensive than fixed roof tanks and this consideration would have to be factored in on any design decision. Pollution control on fixed roof tank vents can achieve even higher removal percentages (90– 98%), but would require annual operating costs in addition to the capital costs of their installation.

Summary

This section presented the major types of storage tanks used in the petroleum and chemical manufacturing industries and their main characteristics. Pollutant generation and release mechanisms were discussed as well as emission reduction techniques, including pollution prevention and control. Significant emission reductions can be achieved by using floating roof storage tanks rather than fixed roof tanks in process design. The costs and benefits of using the more expensive floating roof tanks must be weighed against pollution control measures placed on the less expensive fixed roof tanks in order to reach a final decision.

Section 4.2: Questions for Discussion

1. **The color of tank paint and it's condition are important parameters in determining emission rates from storage tanks. Discuss the relevance of tank paint color and paint condition considering the emission mechanisms discuss above.**
2. **How much net emission reduction can be expected if a Grey/Medium color (poor condition) fixed roof tank (same as in example problem 9.1) is painted white? Assume that the paint is an oil based paint with 50% by volume toluene solvent inside and that one gallon covers 100 square feet of tank external surface. Assume that the dome roof is flat for this calculation.**

III. Reactor Pollution Prevention

Reactors are the most important unit operation in a chemical process from an environmental perspective. The degree of conversion of feed to desired products influences all subsequent separation processes, recycle structure for reactors, waste treatment options, energy consumption, and ultimately pollutant releases to the environment. Once a chemical reaction pathway has been chosen, the inherent product and byproduct (waste) distributions for the process are to a large extent established. However, the synthesis must be carried out on an industrial scale in a particular reactor configuration and under specified conditions of temperature, pressure, reaction media (or solvent), mixing, and other aspects of the reactor operation. There are many pollution prevention considerations and opportunities for reactors in chemical processes. For this discussion, these considerations will be classified as 1) Material Use and Selection, 2) Reaction Type and Reactor Choice, and 3) Reactor Operation.

In the following discussion, we will focus on reactor operation and a risk-based method using the US EPA OPPT tools to optimize chemical reactions and reactors. An example application deals with choosing residence time in a fluidized bed reactor for the production of acrylonitrile.

There are many ways to calculate environmental risks posed by chemicals. Chapter 11 presents a comprehensive method to generate environmental impact and human health metrics. Simplified metrics would be useful for screening byproducts generated in chemical reactors. Decisions regarding optimum reactor operation could then be made based on the risks posed by the individual byproducts generated rather than on just the mass rate of generation of each component. Using the Waste Minimization Prioritization Tool (US EPA WMPT, 1999) methodology as a guide, we can use the following definition of risk in this development. The basis for the risk definition is the bioaccumulation of persistent toxic chemicals in the fatty tissue of animals in the upper trophic levels of the food chain.

Risk = Toxicity x Exposure

Exposure = F x Mass x Persistence x Bioaccumulation

where

Toxicity = the Reference Dose (RfD) for ingestion exposure route.

F = the fraction of the byproduct that enters the environment from wastewater treatment. This is determined by the OPPT tool EPIWIN.

Mass = the mass rate of byproduct generation in the reactor. This is a function of reactor conditions (temperature, residence time, mixing etc.). This is predicted by a model of the reactor system.

Persistence = the biodegradation timeframe. This is determined by the OPPT tool BIODEG if no data is available.

Bioaccumulation = the Bioconcentration Factor (BCF) of the compound. BCF of a chemical is the fraction partitioned into fatty tissue of an animal versus dissolved in water. BCF is calculated using the OPPT tool EPIWIN if no data is available.

Example Problem 9.2 Acrylonitrile Reactor (Hopper et al. 1992)
Risk-Based Input-Output Analysis of a Reactor.
Acrylonitrile is produced in a fluidized bed reactor containing a catalyst (Bi-Mo-O). The main reaction for acrylonitrile is ammonoxidation represented by

$$\underset{\text{propylene}}{CH_2{=}CH{-}CH_3} + \underset{\text{ammonia}}{NH_3} + \underset{\text{oxygen}}{3/2\ O_2} \rightarrow \underset{\text{acrylonitrile}}{CH_2{=}CH{-}CN} + \underset{\text{water}}{3H_2O}$$

In addition there are five other possible side reactions including

$$CH_2{=}CH{-}CH_3 + O_2 \rightarrow \underset{\text{acrolein}}{CH_2CH{-}CHO} + H_2O$$

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

$$CH_2CH{-}CHO + NH_3 + 1/2\ O_2 \rightarrow CH_2{=}CH{-}CN + 2H_2O$$

$$CH_2{=}CH{-}CN + 2\ O2 \rightarrow CO_2 + CO + HCN + 3H_2O$$

hydrogen cyanide

Hooper and coworkers (Hooper et al. 1992) constructed a fluidized bed reactor (FBR) model for above set of chemical reactions assuming first order reaction kinetics with respect to the reactant, product, and byproduct species. The model also includes mole balance and energy balance equations for the reactor. The model was used to predict the effects of reaction temperature, residence time, and reactor type (constant stirred tank reactor (CSTR), plug flow reactor (PFR), and FBR) on the generation of reaction byproducts in the acrylonitrile reaction. Here, we will illustrate the use of the FBR model predictions in determining the optimum residence time for minimum waste generation. The evaluation will be based on both mass generation as well as and risk generation approaches.

The predicted concentrations of product and byproduct species from the reactor as a function of reactor residence time are shown in Figure 9.6-1. These results show that acrylonitrile concentration increases with residence time up to about 10 seconds. Thereafter, the increase in acrylonitrile concentration is more slow and after 15 seconds, there is no further increase in concentration. Reactant (propylene) continues to decline with increasing reactor residence time due to conversion of the reactant to product and byproduct species. Byproducts, hydrogen cyanide (HCN) and acetonitrile, exhibit complex profiles with respect to residenct time. HCN is only generated in significant amounts above about 5 seconds residence time. HCN is the dominant reaction byproduct at higher resedence times. Acetonitrile is generated in higher amounts than HCN at low residence times, but tends to level off and remain at a relatively constant concentrations as residence time increases to 20 seconds. Based on these results, the authors (Hopper et al. 1992) recommended to operate the reactor at a temperature of 400 – 480 ˚C, a reactor residence time of 2 – 10 seconds, and to use a fluidized bed reactor.

A presentation of the same reactor results on a risk basis is shown in Figure 9.6-2. In this figure, the mass generation rates of byproducts were converted to a risk generation rate by using the WMPT methodology outlined above. The risk parameters used in the conversion of mass to risk basis is shown in Table 9.6-1.

Table 9.6-1 Risk parameters for byproducts in the acrylonitrile reaction.

Chemicals	Removal Efficiency (%)	Toxicity, Reference Dose (mg/kg/d)	Persistence, Biodegradation Lifetime (d)	Bioaccumulation (BCF)
HCN	90.51	0.02	5	3.16
Acetonitrile	3.67	0.006	5	3.16

The risk parameters shown in Table 9.6-1 confirm that both byproducts are highly toxic and that acetonitrile is about three time more toxic than HCN. Also, only 3.67% of the acetonitrile is expected to be removed in a wastewater treatment plant and therefore should have a much higher ingestion exposure potential than HCN, which is removed with about a 90.5% efficiency (mostly due to volatilization to air). These risk parameters indicate that acetonitrile is much more of a concern than HCN in terms of *ingestion* human health risks. This same conclusion is illustrated in Figure 9.6-2, where the risk index is plotted for each byproduct versus reactor residence time. The rate of risk generation for acetonitrile is much larger than for HCN, even though the mass rate of HCN generation is ultimately larger. The risk based approach would lead the design engineer to focus on minimizing acetonitrile generation in the reactor, and may well lead to a different optimum reactor configuration than if the optimization were based on byproduct mass generation rates only.

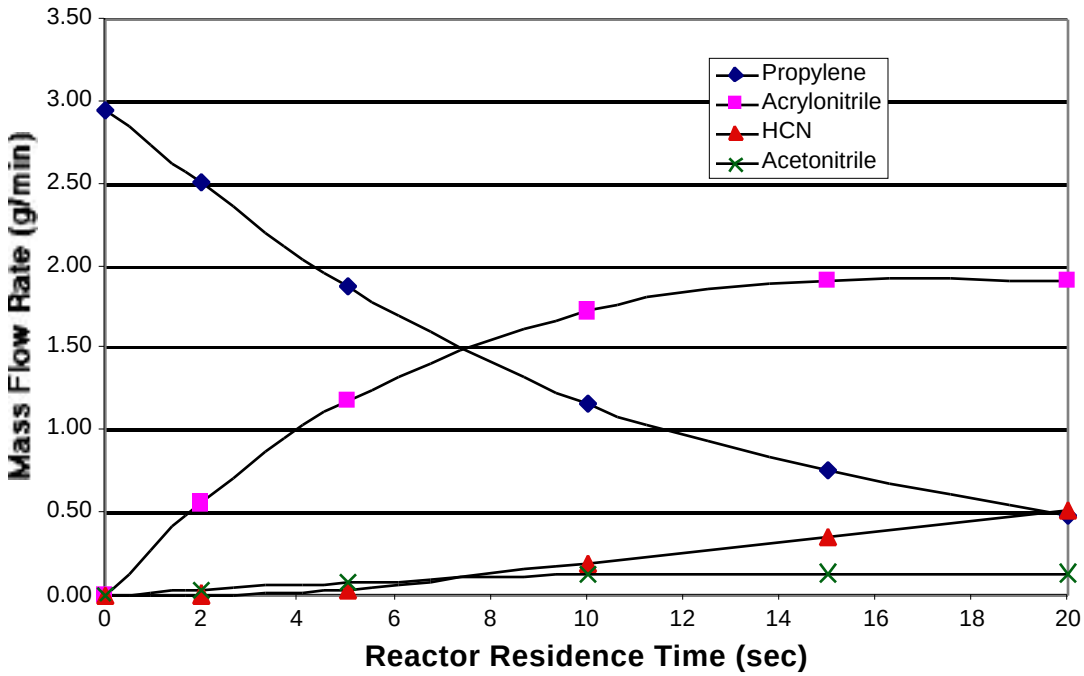

Figure 9.6-1 Effect of reactor residence time on the conversion of propylene to product (acrylonitrile) and byproducts (hydrogen cyanide, HCN and acetonitrile). The model is of a fluidized bed reactor at 400 ˚C. Byproduct generation is shown on a mass basis.

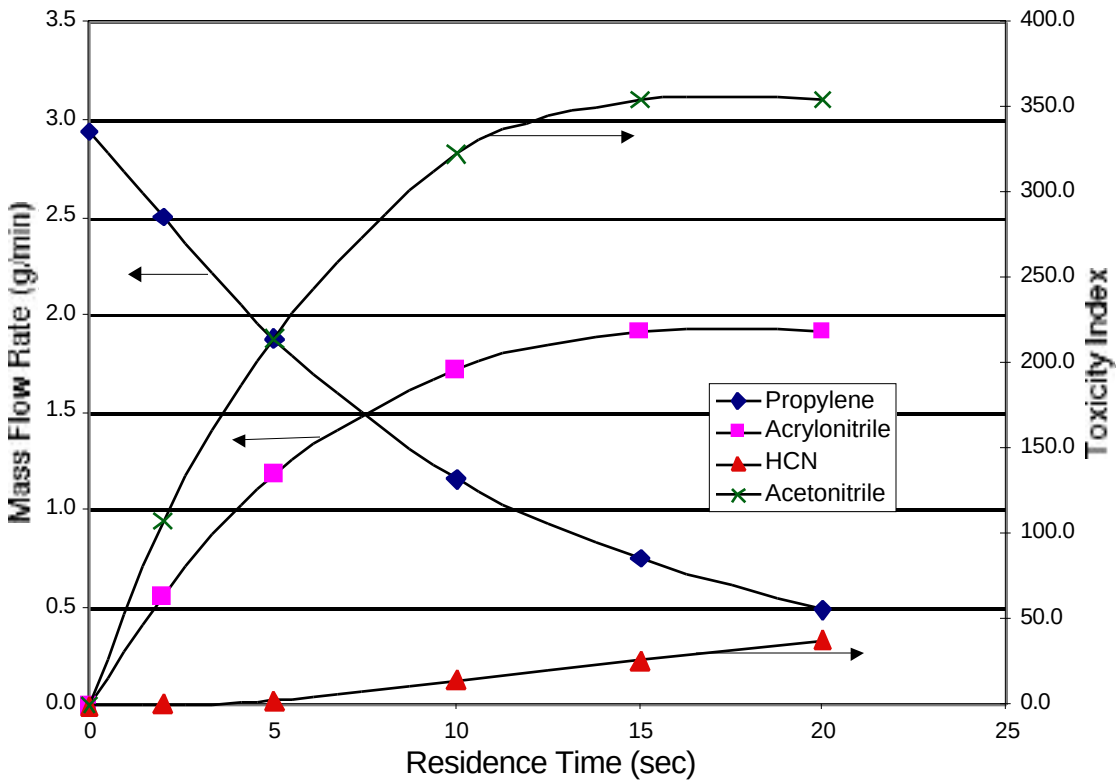

Figure 9.6-2 Effect of reactor residence time on the conversion of propylene to product (acrylonitrile) and byproducts (hydrogen cyanide, HCN and acetonitrile). The model is of a fluidized bed reactor at 400 ˚C. Byproduct generation is shown on a risk basis.

Summary

This section illustrated the use of a risk-based approach for deciding upon optimum reactor operating conditions. Using the acrylonitrile reaction in a fluidized bed reactor as an example, the mass-based approach indicated that avenues to minimize HCN generation should be the focus of pollution prevention efforts. The risk based approach indicated that acetonitrile minimization should be the focus of this effort. This example illustrated the benefits of including risk screening in pollution prevention efforts involving reactors.

Section 4.2: Questions for Discussion

1. The risk-based approach presented in this section used several environmental and toxicological parameters. Briefly discuss the relevance of each parameter in the risk calculation. Why is the inclusion of each parameter important? For example, what does the use of bioaccumulation in the risk calculation imply about the route of exposure? What is being ingested that caused the health concern?

References

API, American Petroleum Institute, “Waste Minimization in the Petroleum Industry: A compendium of Practices”, API Publication 849-00020, Washington, DC, 1991a.

API, American Petroleum Institute, “The Generation and Management of Wastes and Secondary Materials in the Petroleum Refining Industry: 1987-1988”, API Publication 4530, Washington, DC, 1991b.

Hooper, J.R., Yaws, C.L., Ho, T.C., Vichailak, M., and Muninnimit, A., Waste minimization by process modification, in Industrial Environmental Lchemistry, Sawyer, DT., and Martell, A.E. ed., Plenum Press, New York, NY, pg 25 – 43, 1992

U.S. EPA TTN, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Technology Transfer Network web site, TANKS4.0 storage tank emission estimation program, http://www.epa.gov/ttn/chief/tanks.html, June 1, 1999.