Chapter 9. Unit Operations and Pollution Prevention

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In developing a flowsheet for the production of a chemical, it is desirable to consider the environmental ramifications of using 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, the improved design will require lower waste treatment and environmental compliance costs and will convert a higher percentage of raw materials into salable product.

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

1. Material Selection: Many of the environmental concerns can be addressed by reviewing material properties and making the correct choice of unit operation and operating conditions. The materials used in each unit operation should be carefully considered so as to minimize the human health impact and environmental damage 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 toward environmentally sound material choices and other pollution prevention options.
3. Operating Conditions: The operating conditions of each unit should be optimized in order to achieve maximum reactor conversion and separation efficiencies.
4. Material Storage and Transfer: The best material storage and transfer technologies should be considered in order to minimize releases of materials to the environment.
5. Energy Consumption: Energy consumption in each unit should be carefully reviewed so as to reasonable 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 the following sections, we apply this framework for preventing pollution in unit operations by considering choices in materials, technology selection, energy consumption, and safety ramifications. In Section 9.2, material choices that are generic to most chemical processes, like process water and fuel type, are analyzed with respect to in-process waste generation and emission release. Other process materials that are more specific to various unit operations are discussed in subsequent sections of this chapter. Chemical reactors are the topic in Section 9.3.The environmental issues related to the use of reactants, diluents, solvents, and catalysts are discussed first. Then, the effects of reaction type and order on product yield and selectivity are covered. The effects of reaction conditions (temperature and mixing intensity) on selectivity and yield are illustrated. Finally, the benefits of additional reactor modifications for pollution prevention are tabulated. In Section 9.4, the most important topics include the choice of material (mass separating agent) to be used in separations, design heuristics, and examples of the use of separation technologies for recovery of valuable components from waste streams, leading eventually to their reuse in the process. Separative reactors are the topic of discussion in Section 9.5. These hybrid unit operations have special characteristics to help achieve higher conversions and yields in chemical reactors compared to conventional reactor configurations. In Section 9.6, methods for reducing emissions from storage tanks and fugitive sources are discussed. The safety aspects of pollution prevention and unit operations are the topic of Section 9.7.It will be shown that many pollution prevention efforts tend to make chemical processes more complex, necessitating a higher level of safety awareness.

In making pollution prevention decisions that include choices of materials, unit operations technologies, operating conditions, and energy consumption, it is very important to consider health and environmental risk factors. It is also of high importance to incorporate cost factors and safety ramifications. In Section 9.8, review a method for evaluating health risk into unit operations decisions by considering the optimum reactor operating conditions as an example application. Although no generally accepted method exists for these risk assessments, the method outlined in Chapter 8 and applied in Section 9.8 is useful for incorporating multiple risk factors into decisions regarding item operations.

Finally, it is also important to introduce the concept of “risk shifting.” 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 for conserving water resources at chemical manufacturing facilities is to employ cooling towers. Process water used for cooling purposes can be recycled and reused many times. However, there is an increased risk to workers who may be exposed to the biocides used to control microbial growth in the cooling water circuit. 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.

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 reducing fugitive emissions is to reduce the number of these units by eliminating backup units and redundancy. This strategy will reduce routine air releases but will increase the probability of a 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 risk from one type to another.

Example problem 9.3-3
Estimate the magnitude of the mixing effect on reaction yield.

A second-order competitive-consecutive reaction is being carried out in a CSTR. The initial concentration of reactant A in the vessel is 0.2 gmole/liter and the feed containing reactant B is introduced into the reactor at the impeller. The volume of the vessel is 100 liters, the impeller diameter is 0.5 ft, k_1 is 35 liter / (gmole•sec), impeller speed is 200 rpm. Additional data is shown below. Estimate the reaction yield as a fraction of the expected yield.

Additional Data:

$L_f = 0.5$ *ft (impeller diameter for feed at impeller tip)*

n = *kinematic viscosity of mixture = 1.08 cs =* $1.16x10^{-5}$ *ft*^{2}*/sec***Solution**The x-axis in Figure 9-3.6 requires that t be calculated, and t requires *u'*.

$$u' = 0.45\, p\, D N = 0.45\, p\, (0.5)(200\ /\ 60) = 2.36 \text{ ft/sec}$$

$$t = 0.882 \frac{n^{3/4}\, L_f^{\ 3/4}}{u'^{\ 7/4}} = 0.882 \frac{(1.16 \times 10^{-5})^{3/4} (0.5)^{\ 3/4}}{(2.36)^{\ 7/4}} = 2.32 \times 10^{-5} \text{ sec}$$

$(k_1 B_o t)(A_o / B_o) = (k_1 t A_o) = (35)(2.32 \times 10^{-5})(0.2) = 1.62 \times 10^{-4}$ From Figure 9-3.7, the estimated value of *Y*/*Y*$_{exp}$ is approximately 0.94. Thus, the mixing in this reactor is almost sufficient to achieve the expected yield. Byproduct generation is not affected to a large degree by mixing in this CSTR, but could be improved slightly by operating the mixer at higher speeds.

Chapter 9 Sample Homework Problem

1. **Solvent Choice for Caffeine Extraction from Coffee Beans**
   About 20% of the coffee consumed in the United States is decaffeinated. There are many solvents and processes developed over the past century to accomplish this step. Critical issues in choosing a solvent are the caffeine/solvent affinity, the cost of the solvent, the ease of caffeine recovery from the solvent, safety aspects, and environmental impacts. The original process used a synthetic organic solvent to extract caffeine from un-roasted coffee beans. These solvents included trichloroethylene

(C_2HCl_3) and methylene chloride (CH_2Cl_2). Today, caffeine is extracted using "natural" solvents including supercritical carbon dioxide, ethyl acetate (naturally found in coffee), oils extracted from roasted coffee, and water. Using Material Safety Data Sheets as a source of information, rank order these solvent candidates based only on their toxicological properties. Do not consider the "extracted oils" since the identity of these is not available. Use PEL and/or LD_{50} (rat) toxicological data.

Information Source on Coffee Extraction: "Encyclopedia of Chemical Technology", Volume 6, Coffee chapter, John Wiley and Sons , 1991 (4th edition) and 1978 (3rd edition).