Green Engineering - the environmentally conscious design and commercialization of processes and products

Textbook Outline

Part I: A Chemical Engineer's Guide to Environmental Issues and Regulations: This section provides an overview of major environmental issues, and an introduction to environmental legislation, risk management and risk assessment.

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- The Role of Chemical Process and Chemical Products
- An Overview of Major Environmental Issues
- Global Environmental Issues
- Air Quality Issues
- Water Quality Issues
- Ecology
- Natural Resources
- Waste Flows in the United States

2. Risk Concepts
- Description of Risk
- Value of Risk Assessment in the Engineering Profession
- Risk-Based Environmental Law
- General Overview of Risk Assessment Concepts
- Hazard Assessment
- Dose-Response
- Exposure Assessment
- Risk Characterization

3. Environmental Law and Regulations: from End-of-Pipe to Pollution Prevention
- Nine Prominent Federal Environmental Statutes
- Evolution of Regulatory and Voluntary Programs: from End-of-Pipe to Pollution Prevention
- Pollution Prevention Concepts and Terminology

4. The Roles and Responsibilities of Chemical Engineers
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Part II: Evaluating and Improving Environmental Performance of Chemical Process Designs: This section will describe a variety of analysis tools for assessing and improving the environmental performance of chemical processes. The group of chapters will begin at the molecular level, and then proceed to an analysis of process flowsheets.

5. Evaluating Environmental Fate: Approaches based on Chemical Structure
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- Estimating Ecosystem Risks
- Using Property Estimates to Estimate Environmental Fate and Exposure
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- Liability Costs
- Internal Intangible Costs
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PART III: Moving Beyond the Plant Boundary: This section will describe tools for improving product stewardship and improving the level of integration between chemical processes and other material processing operations.

13. Life Concepts, Product Stewardship and Green Engineering
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- Life Cycle Assessments
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- Uses of Life Cycle Studies

14. Industrial Ecology
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Series of Appendices:

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Appendix B - Molecular Connectivity

Appendix C - Estimating Emissions from Storage Tanks

Appendix D - Tables of Environmental Impact Potentials - Tables D1 – D4

Appendix E - Procedures for Estimating Hidden (Tier II) Costs - Tables E1 - E5

Appendix F - Additional Resources - Web Resources/Online Databases/Software

Chapter 1. An Introduction to Environmental Issues

by
David R. Shonnard

Environmental issues gained increasing prominence in the latter half of the 20th century. Global population growth has lead to increasing pressure on worldwide natural resources including air and water, arable land, and raw materials, and modern societies have generated an increasing demand for the use of industrial chemicals. The use of these chemicals has resulted in great benefits in raising the standard of living, prolonging human life and improving the environment. But as new chemicals are introduced into the marketplace and existing chemicals continue to be used, the environmental and human health impacts of these chemicals have become a concern. Today, there is a much better understanding of the mechanisms that determine how chemical are transported and transformed in the environment and what their environmental and human health impacts are, and it is now possible to incorporate environmental objectives into the design of chemical processes and products.

The challenge for future generations of chemical engineers is to develop and master the technical tools and approaches that will integrate environmental objectives into design decisions. The purpose of Chapter 1 is to prsent a brief introduction to the major environmental problems that are caused by the production and use of chemicals in modern industrial societies. With each environmental problem introduced, the chemicals or classes of chemicals implicated in that probem are identified. Whenever possible, the chemical reactions or other mechanisms responsible for the chemical's impact are explained. Trends in the production, use, or release of those chemicals are shown. Finally, a brief summary of adverse health effects is presented. This chapter's intent is to present the broad range of environmental issues which may be encountered by chemical engineers. Chapter 3 contains a review of selected environmental regulations that may affect chemical engineers. It is hoped that this information will elevate the environmental awareness of chemical engineers and will lead to more informed decisions regarding the design, production, and use of chemicals.

Chapter 1 Example Problem

Efficiency of Primary and Secondary Energy: Determine the efficiency of primary energy utilization for a pump. Assume the following efficiencies in the energy conversion;

- crude oil to fuel oil is 90% (0.90)
- fuel oil to electricity is 40% (0.40)
- electricity transmission and distributions is 90% (0.90)

- conversion of electrical energy into mechanical energy of the fluid being pumped is 40% (0.40)

Solution: The overall efficiency for the primary energy source is the product of all the individual conversion efficiencies.

Overall Efficiency = (0.90)(0.40)(0.90)(0.40) = (0.13) or 13%.

Chapter 1 Sample Homework Problem

Electric Vehicles: Effects on Industrial Production of Fuels

Replacing automobiles having internal combustion engines with vehicles having electric motors is seen by some as the best solution to urban smog and tropospheric ozone. Write a short report (1-2 pages double spaced) on the likely effects of this transition on industrial production of fuels. Assume for this analysis that the amount of energy required per mile traveled is roughly the same for each kind of vehicle. Consider the environmental impacts of using different kinds of fuel for the electricity generation to satisfy the demand from electric vehicles. This analysis does not include the loss of power over the lines/grid.

Chapter 2. Risk Concepts

by
Fred Arnold & Gail Froiman
with John Blouin

Risk: the probability that a substance or situation will produce harm under specific conditions. Risk is a combination of two factors: the probability that an adverse even will occur and the consequences of the adverse event.

The Presidential/Congressional Commission
on Risk Assessment & Risk Management, Vol. 1, 1997

Risk is a concept that used in the chemical industry and by practicing chemical engineers. The term risk is multifaceted and is used in many disciplines such as: finance (rate of return for a new plant or capitol project, process improvement, etc), raw materials supply (single source, back integration), plant design and process change (new design, impact on bottom line), and site selection (foreign, political stability). Though the term risk used in these disciplines can be discussed either qualitatively or quantitatively, it should be obvious that these qualitative or quantitative analyses are not fields (financial risk ≠ process change risk). This chapter will focus on the basic concept of environmental risk and risk assessment as applied to a chemical's manufacturing, processing, or use, and the impact of exposure to these chemicals on human health or the environment.

Risk assessment is a systematic, analytical method used to determine the probability of adverse effects. A common application of risk assessment methods is to evaluate human health and ecological impacts of chemical releases to the environment. Information collected from environmental monitoring or modeling is incorporated into models of human or worker activity and exposure, and conclusions on the likelihood of adverse effects are formulated. As such, risk assessment is an important tool for making deisions with environmental consequences. Almost always, when the results from environmental risk assessment are used, they are incorporated into the decision-making process along with economic, societal, technological, and political consequences of a proposed action.

Chapter 2 Example Problem

Example 2.6-3: Reference-Dose

Reference doses are used to evaluate noncarcinogenic effects resulting from exposure to chemical substances. The reference dose (RfD) is the threshold of exposure below which protective mechanisms are believed to guard an oganism from adverse effects resulting from exposure over a substantial period of time. When valid human toxicological data are available, it forms the basis for the reference dose. When human exposure data are not available, the animal species believed to be most sensitive to the chemical of concern is used to determine the lowest level at which an adverse effect is detected, often called the LOAEL. Similarly the NOAEL is the greatest test-dose level at which no adverse effect is noted. When animal data are used the reference dose for human populations is adjusted by extrapolation factors to convert the NOAEL or LOAEL into a human subthreshold or reference dose.

$$RfD = \frac{NOAEL}{F_A F_H F_S F_L F_D}$$

where F_A is an adjustment factor to extrapolate from animal to human populations;
F_H is an adjustment factor for differences in human susceptibility;
F_S is an adjustment factor used when data are obtained from subchronic studies;
F_L is an adjustment factor applied when the LOAEL is used instead of the NOAEL; and,
F_D is an adjustment factor applied when the data set is dubious or incomplete.

Each adjustment factor should account for the systematic difference between the two measures bridged by the extrapolation and incorporate a margin of safety in accordance with the uncertainty associated with the extrapolation. For example, in a 3-month subchronic study in mice, the NOAEL for tris(1,3-dichloro-2-propyl) phosphate was 15.3 mg/kg body weight per day; the LOAEL was 62 mg/kg at which dose abnormal liver effects were noted. *See* Kamata E. et al., Acute and subacute toxicity studies of tris(1,3-dichloro-2-propyl) phosphate on mice. *Bull Natl Inst Hyg Sci*, 107:36-43 (1989). If each of the adjustment factors is equal to 10, the reference dose for this chemical is:

Using the NOAEL:

$$RfD = \frac{NOAEL}{F_A F_H F_S} = \frac{15.3 mg/kg-day}{10x10x10} = 0.015 mg/kg-day$$

Using the LOAEL:

$$RfD = \frac{LOAEL}{F_A F_H F_L F_S} = \frac{62 mg/kg-day}{10x10x10x10} = 0.0062 mg/kg-day$$

The lesser of the two values, 0.0062 mg/kg-day, would be selected as the reference dose for humans in this instance.

Chapter 2 Sample Homework Problem

1. A colleague has requested your advice on selection of a safe solvent for a photoresist. A photoresist consists of an acrylate monomer, polymeric binder, and photoinitiator applied to the surface of a copper-clad laminate or silicon wafer. After the solvent

evaporates, the photoresist is exposed to ultraviolet light through a mask containing the pattern to be etched on the circuit board or silicon wafer. When exposed, the resist polymerizes and becomes insoluble to the developer. The circuit board or silicon wafer is subsequently washed with the developer solution to remove unpolymerized photoresist exposing the pattern to be etched with acid into the copper metal or the silicon wafer. Your colleague has identified the following solvents as suitable for formulation of the photoresist.

Solvent	CAS Number	Vapor Pressure kPa at 25°C	OSHA Concentration Limit (parts per million)
Furfuryl alcohol	98-00-0	0.1	50
Diethylamine	109-89-7	30.1	25
Ethyl acetate	141-78-6	12.6	400
Monomethyl ether	109-86-4	1.3	25
Methyl ethyl ketone	79-93-3	12.1	200
n-butyl acetate	123-86-4	1.3	150

a. Using the OSHA Permissible Exposure Limit as a surrogate for relative hazard, a higher OSHA PEL connoting a lower hazard, rank these solvents from highest hazard to lowest.
b. Using the vapor pressure as a surrogate for the magnitude of worker exposure to the solvent vapors, rank these solvents from highest exposure potential to lowest.
c. Considering both hazard and exposure potential, which of these solvents would you recommend to your colleague for the photoresist solution?
d. What alternatives can be used to reduce the risk associated with solvents even further?

Chapter 3. Environmental Law and Regulations: From End-of-Pipe to Pollution Prevention

by
David R. Shonnard

Chemical engineers practice a profession and must obey rules governing their professional conduct. One important set of rules that all chemical engineers should be aware of is environmental statutes, which are laws enacted by Congress. Regulations are promulgated by administrative agencies based on authority conferred by the statute. The Environmental statutes are designed to protect human health and the environment by placing limits on the quantity and chemical make-up of waste streams that are released from manufacturing processes. For example, one statute places restrictions on how hazardous waste from industry is stored, transported, and treated. Another statute places strict liability on the generators of hazardous waste, requiring responsible parties to clean up disposal sites that fail to protect the environment. For manufacturers of new chemicals, there are regulatory requirements that required filing of a premanufacture notice (PMN) before introducing a new chemical into the marketplace. While many companies have Health, Safety, and Environment (HS&E) staff that can help the engineer interpret and implement environmental requirements, it is nevertheless important that chemical engineers be aware of prominent federal environmental laws, and adhere to the requirements of these statutes.

The purpose of this chapter is to provide an overview of environmental regulation. Much of the material on regulations in this chapter has been adapted from an excellent review of environmental law by Lynch (1995). More comprehensive sources on this topic include the United States Code (U.S.C.), and the Code of Federal Regulations (C.F.R.), which are sets of environmental statutes and regulations, respectively; they are available online at the sited maintained by the federal government printing office. The Environmental Law Handbook (Sullivan and Adams, 1997) and West's Environmental Law Statutes (West Publishing Co.) are compendia of existing statutes. Most of these sources can be found online.

There are approximately 20 federal statutes, hundreds of state and local ordinances, thousands of federal and state regulations, and even more federal and state court cases and administrative adjudications, etc., that deal with environmental issues. Taken together, they make up the field of environmental law, which has seen explosive growth in the last 30 years, as shown in Figure 3.1-1. Chemical engineers should be familiar with environmental laws and regulations because they affect the operation of chemical processes and the professional responsibilities of chemical engineers. *Environmental regulations* and the *common law system* of environmental law require actions by affected entities. For example, the Clean Water Act (an environmental statute) requires facilities that discharge pollutants from a point source into navigable waters in the United States to apply for a national pollutant discharge elimination system (NPDES) permit. In many firms, chemical engineers are responsible for applying for and obtaining these permits. The common law created by judicial decision also encourages chemical engineers to act

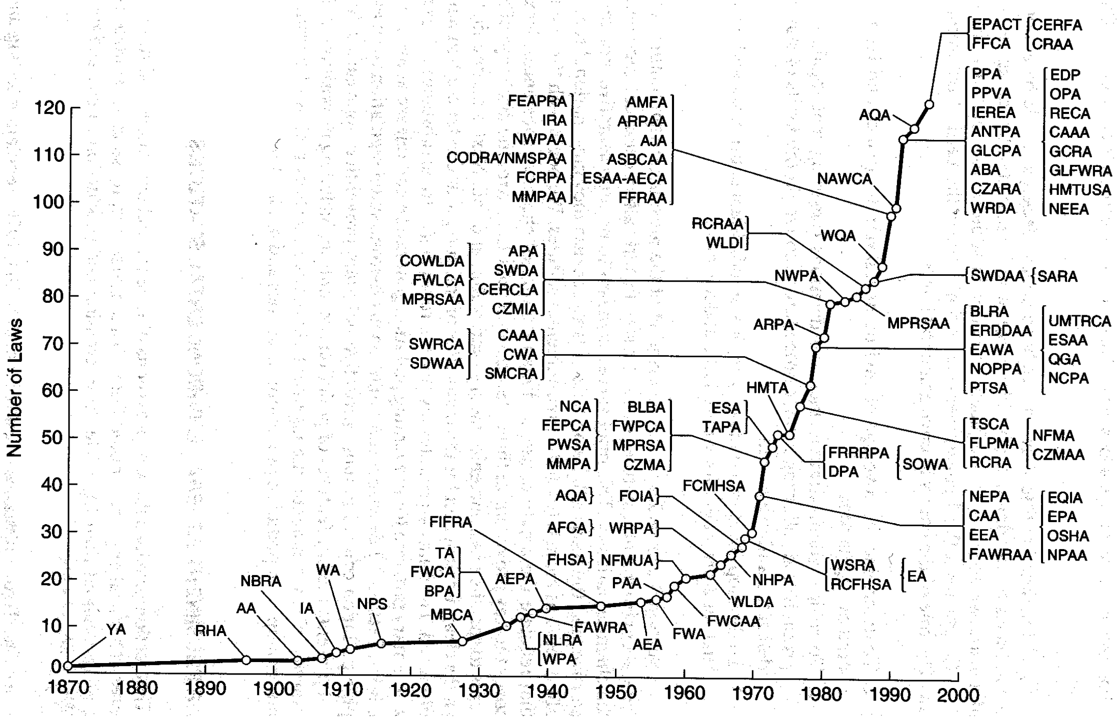


Figure 3.1-1 Cumulative growth in the federal environmental laws and amendments.

responsibly when performing their professional duties because environmental laws and regulation do not cover every conceivable environmental wrong. Chemical engineers need to be aware of the potential legal liability resulting from violation of environmental laws and regulations to protect their company and themselves from legal and administrative actions.

The sources of environmental laws and regulations are legislatures, administrative agencies, and the courts. When drafting environmental laws, federal and state legislatures often use broad language to describe the objectives, regulatory programs, and enforcement provisions of the statute. Often, legislators do not have the time or resources to implement the statute and therefore leave the detailed development of regulations to administrative agencies. Administrative agencies, such as the Environmental Protection Agency, give meaning to statutory provisions through a procedure know as rule making. Federal rule making consists of giving notice of proposed new regulations by publication in the *Federal Register*, providing an opportunity for public comment, altering the proposed rule, where appropriate, to incorporate the comments received, and publishing final regulations in the Federal Register. Final rules have the force of law. As such, administrative agencies fulfill a legislative function delegated to them by Congress.

Administrative agencies can be created by the executive or legislative branches of government. In 1970, President Nixon established the United States Environmental

Protection Agency by executive order to consolidate federal programs for regulating air and water pollution, radiation, pesticides, and solid waste disposal. However, administrative agencies are most often established by statue(for example, the Occupational Safety and Health Act established the Occupational Safety and Health Administration), and in these cases, the agency powers are derived from their enabling legislation. Administrative agencies also have the authority to resolve disputes that arise from the exercise of their administrative powers. Regulated entities have the right to appeal decisions made by administrative agencies to an administrative law judge, who is appointed by the agency. Thus administrative agencies have a judicial function in addition to a legislative function.

Courts are a third government actor that helps to define the field of environmental law. The role of the courts in environmental law is:

1. To det ermine the coverage of environmental statutes (which entities are covered by regulations);
2. To review administrative rules and decisions (ensuring that regulations are promulgated following proper procedures and within the limits of statutorily delegate authority); and
3. To develop the common law (a record of individual court cases and decisions that set a precedent for future judicial decisions).

Section 3.2 provides a brief description of the most important features of nine federal environmental statutes that most significantly affect chemical engineers and the chemical industry. This brief survey is meant to be representative, not comprehensive, and the focus will be on federal laws because they have national scope and often serve as models for state environmental statutes. We begin with three statutes that regulate the creation, use, and manufacture of chemical substances. Next, we cover the key provisions of three statutes that seek to control the discharge of pollutants to specific environmental media — air, water, and soil. Next, a statute that initiated a clean-up program for the many sites of soil and groundwater contamination is discussed. The final two statutes involve the reporting of toxic substance releases and a voluntary program for preventing pollution generation and release at industrial facilities. Section 3.3 describes the evolution in environmental regulation from end-of-pipe pollution control to more proactive pollution prevention approaches. Section 3.4 presents the key features of pollution prevention, including its position in the hierarchy of environmental management alternatives, a short review of terminology, and examples of pollution prevention strategies and applications.

Chapter 3 Example Table

Table 3.1 Summary Table for Environmental Laws

Environmental Statute	Date Enacted	Background	Key Provisions
Regulation of Chemical Manufacturing			
The Toxic Substances Control Act (TSCA)	1976	Highly toxic substances, such as polychlorinated biphenyls (PCBs), began appearing in the environment and in food supplies. This prompted the federal government to create a program to assess the risks of chemicals before they are introduced into commerce.	Chemical manufacturers, importers, or processors, must submit a report detailing chemical and processing information for each chemical. Extensive testing by companies may be required for chemicals of concern. For newly created chemicals, a Premanufacturing Notice must be submitted.
The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	Enacted, 1947 Amended, 1972	Because all pesticides are toxic to plants and animals, they may pose an unacceptable risk to human health and the environment. FIFRA is a federal regulatory program whose purpose is to assess the risks of pesticides and to control their usage so that any exposure that my result poses an acceptable level of risk.	Before any pesticide can be distributed or sold in the U.S., it must be registered with the EPA. The data is difficult and expensive to develop and must prove that the chemical is effective and safe to humans and the environment. Labels must be placed on pesticide products that indicate approved uses and restrictions.
The Occupational Safety and Health Act (OSH Act)	1970	The agency that oversees the implementation of the OSH Act is the Occupational Safety and Health Administration (OSHA). All private facilities having more than 10 employees must comply with the OSH Act requirements.	Companies must adhere to all OSHA health standards (exposure limits to chemicals) and safety standards (physical hazards from equipment). The OSH Act's Hazard Communication Standard requires companies to develop hazard assessment data (material safety data sheet (MSDS), label chemical substances, and inform and train employees in the safe use of chemicals.

Table 3.1 Continued; Summary Table for Environmental Laws

Environmental Statute	Date	Background	Key Provisions
Regulation of Discharges to the Air, Water, and Soil			
Clean Air Act (CAA)	1970	The CAA is intended to control the discharge of air pollution by establishing uniform ambient air quality standards that are in some instances health-based and in others, technology-based. The CAA also addresses specific air pollution problems such as hazardous air pollutants, stratospheric ozone depletion, and acid rain.	The CAA established the National Ambient Air Quality Standards (NAAQS) for maximum concentrations in ambient air of CO, Pb, NO_2, O_3, particulate matter, and SO_2. States must develop source-specific emission limits to achieve the NAAQS. States issue air emission permits to facilities. Stricter requirements established for hazardous air pollutants (HAPs) and for new sources.
Clean Water Act (CWA)	1972	The Clean Water Act (CWA) is the first comprehensive federal program designed to reduce pollutant discharges into the nation's waterways ("zero discharge" goal). Another goal of the CWA is to make water bodies safe for swimming, fishing, and other forms of recreation ("swimmable" goal). This act is considered largely successful because significant improvements have been made in the quality of the nation's waterways since its enactment.	The CWA established the National Pollutant Discharge Elimination System (NPDES) permit program that requires any point source of pollution to obtain a permit. Permits contain either effluent limits or require the installation of specific pollutant treatment. Permit holders must monitor discharges, collect data, and keep records of the pollutant levels of their effluents. Industrial sources that discharge into sewers must comply with EPA pretreatment standards by applying the best available control technology (BACT).
Resource Conservation and Recovery Act (RCRA)	1976	The Resource Conservation and Recovery Act was enacted to regulate the "cradle-to-grave" generation, transport, and disposal of both non-hazardous and hazardous wastes to land, encourage recycling, and promote the development of alternative energy sources	Generators must maintain records of the quantity of hazardous waste generated, where the waste was sent for treatment, storage, or disposal, and file this data in biennial reports to the EPA. Transporters and disposal facilities must adhere to similar requirements for record keeping as well as for monitoring the environment.

		based on solid waste materials.	

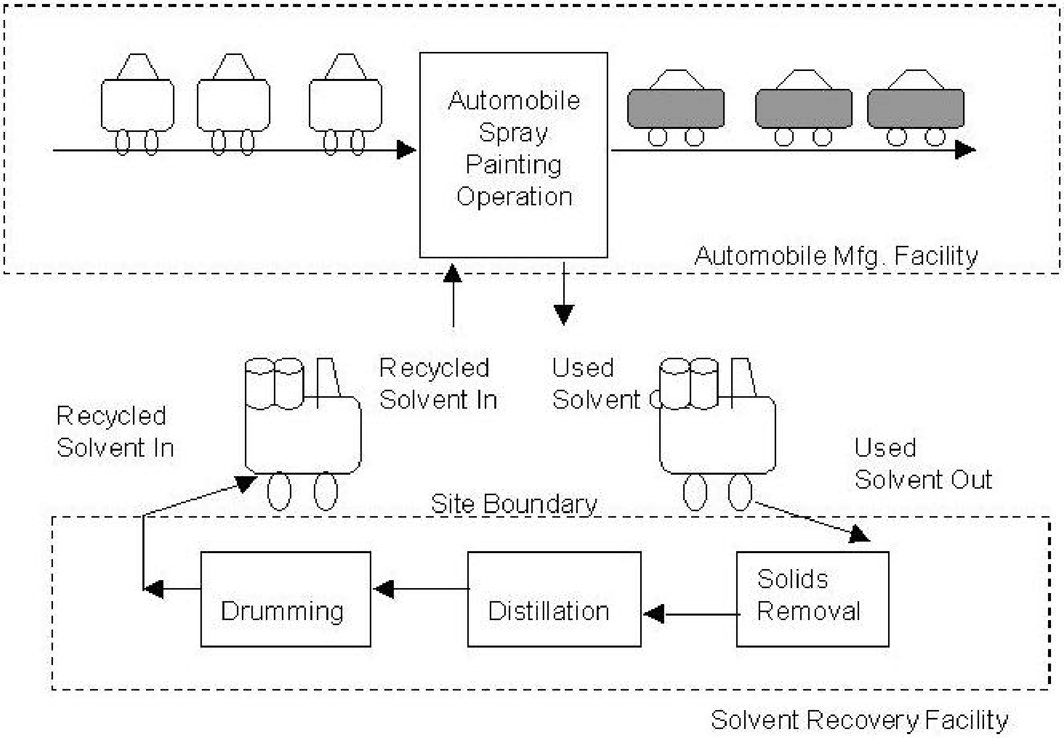
Table 3.1 Continued; Summary Table for Environmental Laws

Environmental Statute	Date Enacted	Background	Key Provisions
Clean-Up, Emergency Panning, and Pollution Prevention			
The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)	1980	CERCLA began a process of identifying and cleaning up the many sites of uncontrolled hazardous waste disposal at abandoned sites, industrial complexes, and federal facilities. EPA is responsible for creating a list of the most hazardous sites of contamination, which is termed the National Priority List (NPL). It was amended by the Superfund Amendments and Reauthorization Act (SARA) of 1986.	After a site is listed in the NPL, EPA identifies potentially responsible parties (PRPs) and notifies them of their potential CERCLA liability, which is strict, joint and several, and retroactive. PRPs are 1) present or 2) past owners of hazardous waste disposal facilities, 3) generators of hazardous waste, and 4) transporters of hazardous waste.
The Emergency Planning and Community Right to Know Act (EPCRA)	1986	Title III of (SARA) contains a separate piece of legislation called the (EPCRA). There are two main goals of EPCRA; 1) to have states create local emergency units that must develop plans to respond to chemical release emergencies, and 2) to require EPA to compile an inventory of toxic chemical releases to the air, water, and soil from manufacturing facilities.	Facilities must work with state and local entities to develop emergency response plans in case of an accidental release. Affected facilities must report annually to EPA data on the maximum amount of the toxic substance on-site in the previous year, the treatment and disposal methods used, and the amounts released to the environment or transferred off-site for treatment and/or disposal.
Pollution Prevention Act (PPA)	1990	The act established pollution prevention as the nation's primary pollution management strategy with emphasis on source reduction. Established a Pollution Prevention Information Clearinghouse whose goal is to compile source reduction information and make it available to the public.	The only mandatory provisions of the PPA requires owners and operators of facilities that are required to file a Form R under the SARA Title III to report to the EPA information regarding the source reduction and recycling efforts that the facility has undertaken during the previous year.

Chapter 3 Sample Homework Problem

1. Categorize the following solvent recovery operation in terms of the waste management hierarchy. Discuss the pollution prevention features of this process. Determine whether this process is pollution prevention or not. Use both the federal definition and also the expanded definition adopted in this text.

Process Description: The automotive industry uses robots to paint automobile bodies before attaching them to the chassis, and installing other components such as the drive train, lights, trim, and upholstery. In order to accommodate different colors, the paint lines must be flushed with a solvent and then re-charged with the new color paint. In the past, this solvent and paint residue was disposed of as hazardous waste or incinerated. The current process of spray painting automobiles uses a closed-loop solvent recovery process as outlined in the diagram below (Gage Products, Ferndale, MI).



Chapter 4. The Roles and Responsibilities of Chemical Engineers

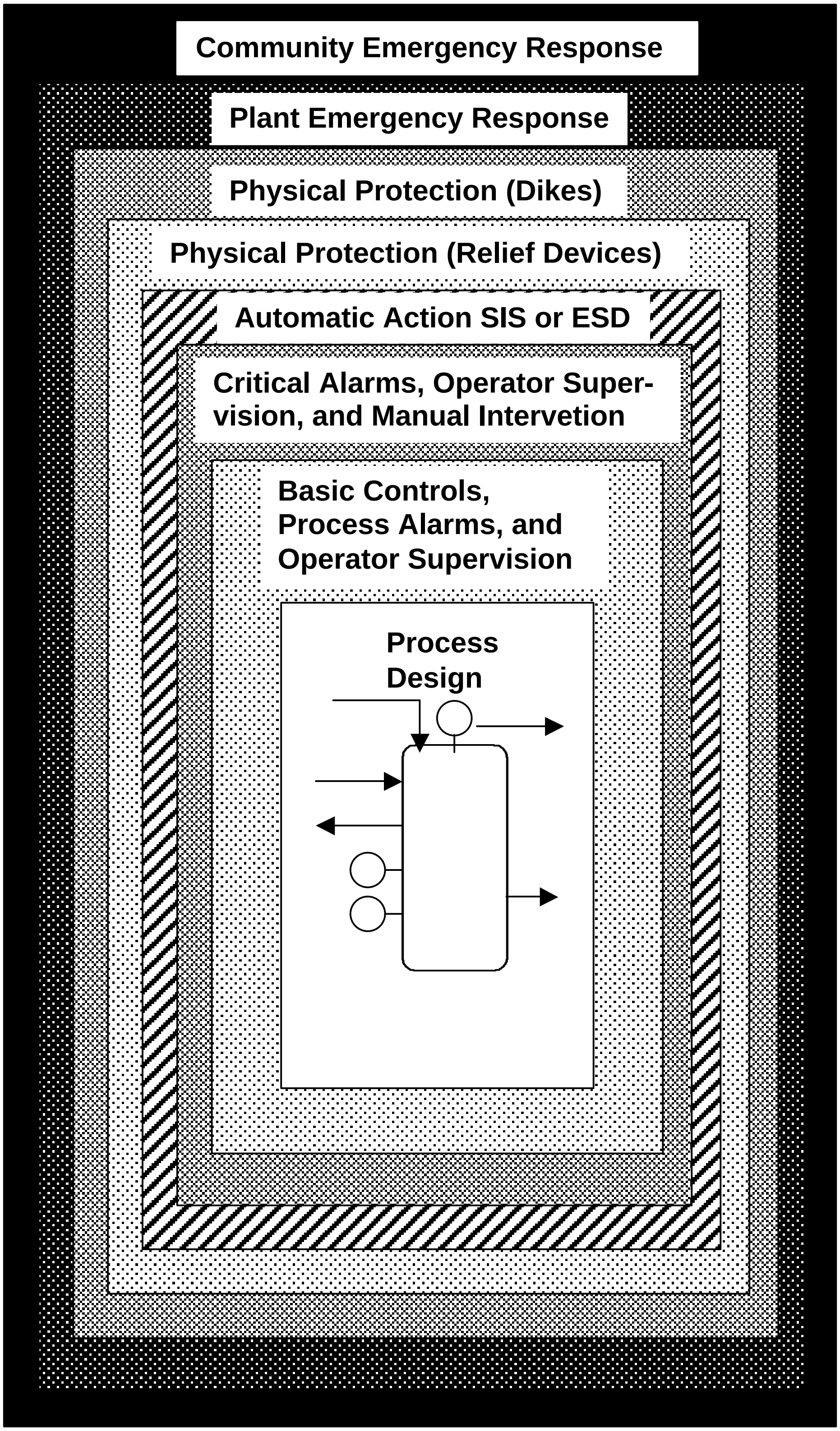
by
David R. Shonnard

Many chemical engineers design and operate large-scale and complex chemical production facilities to supplying diverse chemical products to society. In performing these functions, a chemical engineer will likely assume a number of roles during a career. The engineer may become involved in raw materials extraction, intermediate materials processing, or production of pure chemical substances; in each activity, the minimization and management of waste stream will have important economic and environmental consequences. Chemical Engineers are involved in the production of bulk and specialty chemicals, petrochemicals, integrated circuits, pulp and paper, consumer products, minerals, and pharmaceuticals. Chemical engineers also find employment in research, consulting organizations, and educational activities. The engineer may perform functions such as process and production engineering, process design, process control, technical sales and marketing, community relations, and management.

As engineers assume such diverse roles, it is increasingly important that they be aware of their responsibilities to the general public, colleagues and employers, the environment, and also to their profession. One of the central roles of chemical engineers is to design and operate chemical processes yielding chemical products that meet customer specifications and that are profitable. Another important role is to maintain safe conditions for operating personnel and for residents in the immediate vicinity of a production facility. Finally, chemical process designs need to be protective of the environment and of human health. Environmental issues must be considered not only within the context of chemical production but also during other stages of a chemical's life cycle, such as transportation, the use of chemicals by customers, recycling activities, and ultimate disposal.

This chapter introduces approaches to designing safe chemical processes (Section 4.2). The point of briefly introducing this important topic is to demonstrate that the evolution of the methods used to design safe processes mirrors the evolution of methods described in this text, which are used to design processes that minimize environmental impacts. Section 4.3 reviews, in slightly more detail, the types of procedures that will be used in designing processes that minimize environmental impacts, and the responsibilities of chemical engineers to reduce poll ution generation within chemical processes. Section 4.4 briefly notes some of the other professional responsibilities of chemical engineers, i.e., issues dealing with engineering ethics.

Chapter 4 Example Figure Typical layers of protection for a chemical plant (CCPS 1993b, Crowl 1996). SIS is safety interlock system and ESD is emergency shutdown.



Chapter 4 Sample Homework Problem

1. Flammability Limits

A vertical fixed-roof storage tank contains pure toluene liquid at a temperature of 25°C in contact with air at the same temperature. The saturation vapor pressure of toluene at this temperature is 0.0374 atm. Assume that the partial pressure of toluene vapor in the air above the liquid achieves this saturation value. You can consider the vapor/air mixture to be an ideal gas. The volume percent of toluene in air can be given by;

$$Vol\,\% = .08205\ \times 10^{-4}\left(\frac{T}{M\,P}\right)C_{Toluene}$$

where T is absolute temperature (K), P is absolute pressure of the air (1 atm), M is the molecular weight of toluene (92.1 g/mole), and $C_{Toluene}$ is the concentration of toluene expressed in mass units (mg toluene/m^3 air).

a) Is the toluene/air mixture a flammability hazard?

b) Below what temperature would the toluene in the storage tank have to be cooled in order that the toluene/air mixture is below the LFL?

Chapter 5. Evaluating Environmental Fate: Approaches Based on Chemical Structure

by
David T. Allen

A new chemical is to be manufactured. Will its manufacture or use pose significant environmental or human health risks? If there are risks, what are the exposure pathways? Will the chemical degrade if it is released into the environment or will it persist? If the chemical degrades will the degradation products pose a risk to the environment?

The challenges involved in answering these questions are formidable. Over 9,000 chemicals are produced commercially and every year, a thousand or more new chemicals are developed. For any chemical, in use there are potential environmental risks to human health and the environment. In general, it will not be possible to rigorously and precisely evaluate all possible environmental impacts. Nevertheless, a preliminary screening of the potential environmental impacts of chemicals is necessary and is possible. Preliminary risk screenings allow businesses, government agencies and the public to identify problem chemicals and to identify potential risk reduction opportunities. The challenge is to perform these preliminary risk screenings with a limited amount of information.

This chapter presents qualitative and quantitative methods for estimating environmental risks when the only hazard information available is a chemical structure. Many of these methods have been developed by the US Environmental Protection Agency (US EPA) and its contractors. The methods are routiney used in evaluating premanufacture notices submitted under the Toxic Substances Control Act (TSCA). Under the provisions of TSCA, before a new chemical can be manufactured in the United States, a premanufacture notice (PMN) must be submitted to US EPA. The PMN specifies the chemical to be manufactured, the quantity to be manufactured and any known environmental impacts as well as potential releases from the manufacturing site. Based on these limited data, the US EPA must assess whether the manufacture or use of the proposed chemical may pose an unreasonable risk to human or ecological health. To accomplish that assessment, a set of tools has been developed that relate chemical structure to potential environmental risks.

Figure 5.1-1 provides a qualitative summary of the processes that determine environmental risks. Table 5.1-1 identifies the chemical and physical properties that will influence each of the processes that determine environmental exposure and hazard. The table makes clear that a wide range of properties need to be estimated to perform a screening level assessment of environmental risks.

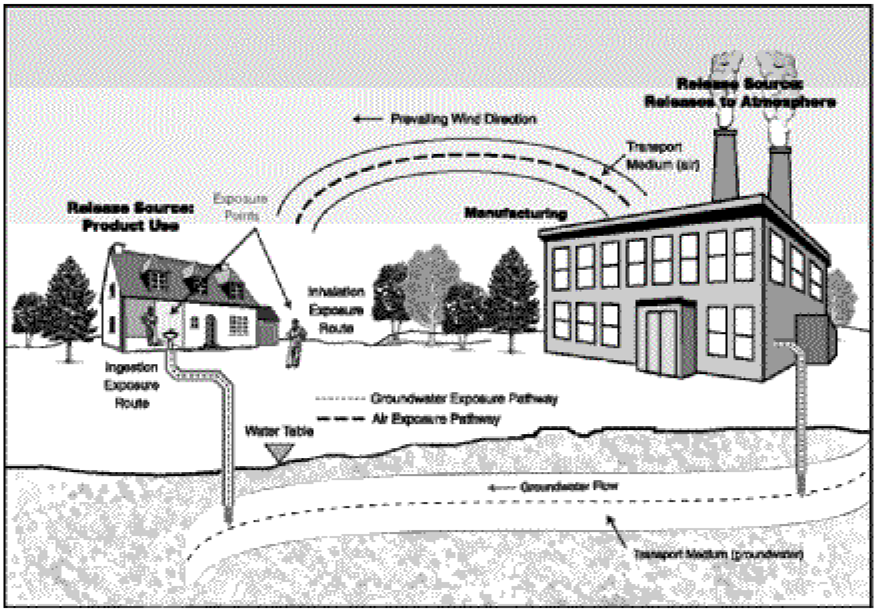


Figure 5.1-1 The chemical and physical properties that will influence each of the processes that determine environmental exposure and hazard.

Table 5.1-1 Chemical Properties Needed to Perform Environmental Risk Screenings

Environmental Process	Relevant Properties
Dispersion and fate	Volatility, density, melting point, water solubility, effectiveness of wastewater treatment
Persistence in the environment	Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation, and adsorption
Uptake by organism	Volatility, lipophilicity, molecular size, degradation rate in organism
Human uptake	Transport across dermal layers, transport rates across lung membrane, degradation rates within the human body
Toxicity and other health effects	Dose-response relationships

The first group of properties that must be estimated in an assessment of environmental risk are the basic physical and chemical properties that describe a chemical's partitioning between solid, liquid and gas phases. These include melting point, boiling point, vapor pressure and water solubility. Additional molecular properties, related to phase partitioning, that are frequently used in assessing the environmental fate of chemicals include octanol-water partition coefficient, soil sorption coefficients, Henry's law constants and bioconcentration factors. (Each of these properties is defined in Section 5.2). Once the basic physical and chemical properties are defined, series of properties that influence the fate of chemicals in the environment are estimated. These include estimates of the rates at which chemicals will react in the atmosphere, the rates of reaction in aqueous environments and the rate at which the compounds will be metabolized by organisms. If environmental concentrations can be estimated based on release rates and environmental fate properties, then human exposures to the chemicals can be estimated. Finally, if exposures and hazards are known, then risks to humans and the environment can be estimated.

The remainder of this chapter describes estimation tools for the properties outlined above. Section 5.2 describes estimation tools for physical and chemical properties. Section 5.3 describes how properties that influence environmental fate are estimated. Methods for estimating hazards to ecosystems are discussed in Section 5.4, and Section 5.5 presents simple models that can be used to characterize the environmental partitioning of chemicals. Finally, Section 5.6 describes how chemical property data can be used to classify the risks associated with chemicals.

Chapter 5 Example Problem

Example 5.2-3

Estimate the vapor pressure at 298 K for toluene (a liquid) and naphthalene (a solid).

Solution

Toluene has the molecular structure CH_3- C_6H_5 and in Example 5.2-1, it's boiling point was estimated to be 399 K. The experimental value for the boiling point is 384 K. We will estimate the vapor pressure using both the predicted and the experimental value for boiling point. Using the predicted value of 399 K:

$$C = -18 + 0.19\ T_b = 57.8$$

$$A = K_F\ (8.75 + R \ln T_b) = 1.0(8.75 + 1.987 * \ln (399)) = 20.6$$

$$\text{Ln } P_{vp} = \frac{[A(T_b - C)^2]}{[0.97\ R\ T_b]}\ [1/(T_b - C) - 1/(T - C)] = \frac{[20.6*(399-57.8)^2]}{[0.97*1.987*399]}\ [1/341 - 1/240]$$

$$\text{Ln } P_{vp} = -3.83; \quad P_{vp} = 0.021 \text{ atm} = 16 \text{ mm Hg}$$

Repeating the calculation for the predicted boiling point leads to a vapor pressure estimate of 19 mm Hg.

<u>Naphthalene</u> has the formula $C_{10}H_8$ and is a solid with a melting point of 81 °C. The boiling point can be estimated from the methods described earlier in this section. The uncorrected group contribution estimate is:

$$T_b = 198.2 + 2(45.46) + 8(28.53) = 517\ \text{K}$$

The corrected value is: $T_b = 505$ K

Applying Equation 5-10:

$$\ln P = -(4.4 + \ln T_b)[1.803\ (T_b/T - 1) - 0.803\ \ln(T_b/T)] - 6.8\ (T_m/T - 1)$$

$$\ln P = -(4.4 + \ln 505)[1.803\ (505/298 - 1) - 0.803\ \ln(505/298)] - 6.8\ (354/298 - 1)$$

$$P = 4.4 * 10^{-5}\ \text{atm} = 0.03\ \text{mm Hg}$$

Chapter 5 Sample Homework Problem

1. Estimate the properties listed in the table given below.

Property	*ethanol*	*1-propanol*	*1-hexanol*	*n-propane*	*n-hexane*
Boiling point (T_b)					
Vapor pressure (P_{vp})					
Henry's Law constant (H)					
Octanol-water partition coefficient (K_{ow})					
Water solubility (S)					
Soil sorption coefficient (K_{oc})					
Atmospheric half life					
Biodegradability					

Chapter 6. Evaluating Exposures

by
Fred Arnold

The human health risk associated with a chemical is dependent on the rate at which the chemical is released, the fate of the chemical in the environment, human exposure to the chemical, and human health response resulting from exposure to the chemical. In simpler terms, as described in Chapter 2, risk is a function of hazard (or toxicity) and exposure. Chapter 5 discusses methods of predicting physical-chemical properties from chemical structure to infer the fate of a chemical in the environment. Chapter 7 discusses green chemistry techniques to select chemical that are less toxic. Chapters 5 and 7 are useful in designing chemical structures with low hazard, on of the two components of the risk equation. This chapter, Chapter 6, addresses the e*xposure* component of the risk equation. Ideally, exposure is quantified by monitoring the work area or environmental setting where a chemical will be used or released; however, when monitoring data are not available to measure exposures, exposures can be estimated using methods described in this chapter.

The methods for estimating exposure will be separated into two sections—occupational and community. Occupational exposure occurs in the workplace. Workers in chemical production facilities may be exposed to toxins used or produced in the chemical process. Exposure to chemicals may occur from the inhalation of workplace air, ingestion of dust or contaminated food, or from contact of the chemical substance with the skin or eyes. In addition, chemical engineers must be aware of community exposures resulting from releases into the air and water, and from solid and hazardous waste disposal. Chemical releases to rivers, lakes, and streams may accumulate in fish and oher marine life, which are subsequently used as a source of food, or may be ingested by persons using the downstream reaches of rivers as a supply of potable water. Persons living downwind of a chemical manufacturing facility may be exposed to fugitive and point source releases of chemical toxins to the atmosphere. Disposal of solid and hazardous wastes on the land, either in repositories such as landfills or into the subterranean strata by injection into wells may result in contamination of potable groundwater if the waste is not isolated form the water supplies.

The intent of Chapter 6 is to introduce students to some methods for predicting potential exposure, in particular, occupational exposure and community exposure. During process design, it may be useful to predict potential exposures to nearby residents from chemical emissions or releases from the plant (i.e., “occupational exposure”), or potential exposures to nearby residents from chemical emission or releases from the plant (i.e., “community pr general population exposure”). There are other exposure areas, such as consumer exposure, which are not discussed in this chapter. The chemical engineer, in addition to selecting chemical with low toxicity, also needs to select solvent chemicals and design unit operations to minimize potential exposure as well.

There are many good references on exposure assessment. Interested students are encouraged to consult references on other types of exposure not covered in this chapter. EPA has a website specifically for exposure which contains computerized tools for all exposure areas (http://www.epa.gov/oppt/exposure). This information can be useful in selecting and designing unit operations. Many of these references are listed in Appendix F.

Chapter 6 Example Problem

Example 6.2-1

A cleaning bath for electronic parts emits 0.5 g/sec of CFC -12 into a small work room of dimensions 3 m x 3 m x 2.45 m high. Calculate the concentration in the room under average and poor ventilation conditions if the air velocity in the room is 0.3 m/s and compare the results to the OSHA PEL.

Solution

When the air speed is 0.3 m/s, the volume of air flowing through the room will be:

Q = 0.3 m/s x 3 m x 2.45 m = 2.21 m3/s,

and the concentration of CFC-12 in the air will be:

average ventilation C = 0.5 g/sec / (0.5 x 2.21 m3/s) = 0.45 g/m3,

poor ventilation C = 0.5 g/sec / (0.1 x 2.21 m3/s) = 2.27 g/m3.

A comparison with the permissible exposure limits given in Table 6.2 -1 indicates that even under poor ventilation conditions, the OSHA PEL will not be exceeded and respiratory protection will not be needed to safe-guard the health of a person working in this room.

Chapter 6 Sample Homework Problem

A liquid transfer pump is leaking at the seals releasing 1 milliliter per minute (about two ounces per hour) of an aqueous solution containing 4 percent acrolein (2-butenal). Nearby, a process tank has a leaking seam from which is weeping an aqueous solution containing 5 percent methyl ethyl ketone (2-butanone) at a rate of 30 milliliters per minute (about 2 quarts per hour). The ventilation rate in the process building where the leaking pump and weeping tank are located is 200 cubic meters per hour. Is either of these releases a potential health hazard to workers in the process building?

Solution:

Because both of these materials are volatile, it can be assumed that the liquids vaporize rapidly. The density of the dilute solutions will be close to that of water, 1000 mg/ml. The average concentration in the process building will be equal to the rate of release of contaminant divided by the ventilation rate. Thus,

For acrolein: $C = (1 \text{ ml/min})(60 \text{ min/hr})(0.04)(1000 \text{ mg/ml})/(200 \text{ m}^3\text{/hr}) = 12 \text{ mg/m}^3$

For MEK: $C = (30 \text{ ml/min})(60 \text{ min/hr})(0.05)(1000 \text{ mg/ml})/(200 \text{ m}^3\text{/hr}) = 450 \text{ mg/m}^3$

Recommendations for short-term exposure limits to environmental contaminants are give in the NIOSH Pocket Guide, available online at www.cdc.gov/niosh/npg/pdgstart.html. For the chemicals in this example, the recommended limits for short-term exposure are 0.8 mg/m for acrolein and 885 mg/m for MEK. Although the exposure to MEK for short periods of time may be acceptable until the weeping tank is repaired, the hazard resulting from short-term exposure to acrolein is unacceptable.

Chapter 7. Green Chemistry

by
Paul T. Anastas and David Allen

Chemical products can be manufactured using a wide variety of synthesis routes. The designer of a chemical process must choose from alternative raw materials, solvents, reaction pathways, and reaction conditions, and these design choices can have a significant impact on the overall environmental performance of a chemical process. Ideal chemical reactions would have attributes such as

- simplicity
- safety
- high yield and selectivity
- energy efficiency
- use of renewable and recyclable reagents and raw materials

In general, chemical reactions cannot achieve all of these goals simultaneously and it is the task of chemists and chemical engineers to identify pathways that optimize the balance of desirable attributes.

Identification of environmentally preferable pathways requires creative advances in chemistry as well as process design. Because the number of choices in selecting reaction pathways is so large and the implications of those choices are so complex, systematic, quantitative design tools for identifying green chemistries are not available. Nevertheless, an extensive body of knowledge concerning green chemistry exists and some qualitative and quantitative design tools are emerging.

Green chemistry, defined as the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances, will be presented in two basic parts - one qualitative and the other quantitative. The first part will describe qualitative principles to be used in developing alternatives - alternative solvents, alternative reactants, alternative chemistries - that may lead to environmental improvements. Section 7.2 provides this overview of qualitative principles that can be used to identify green chemistry alternatives. Section 7.3 describes quantitative, optimization based approaches that have been used to identify environmentally preferable reaction pathways. Finally, Section 7.4 briefly describes the US Environmental Protection Agency's Green Chemistry Expert System, which provides case studies of many of the principles described in this chapter.

Chapter 7 Example Problem

Example 7.1 Calculate atom and mass efficiencies for the Friedel-Crafts reaction shown in Figure 7.5 Assume that the substituent R on the organic chloride is a methyl group.

Solution

To calculate the atom efficiencies, determine the fraction of the carbon, hydrogen, aluminum, chlorine, sodium and oxygen atoms that emerge as product and the fraction that emerges from the reaction as waste.

- Virtually all of carbon (100%) becomes product.
- Most of hydrogen (excluding water in the water wash) becomes product, however if hydrogen used in the water wash is included, virtually all of the hydrogen becomes waste
- All of the aluminum becomes waste (0% efficiency)
- All of the chlorine becomes waste (0% efficiency)
- All of the sodium becomes waste (0% efficiency)
- One mole of oxygen in the organic chloride is inc orporated into the product. Three moles of oxygen is the sodium hydroxide becomes waste. Therefore, excluding oxygen in water, the atom efficiency is 25%.

The mass efficiency can be calculated using atomic weights (ignoring water use).

Mass in product = 8 moles carbon * 12 + 10 moles hydrogen * 1 + 1 mole oxygen * 16 = 122

Mass input = 8 moles carbon * 12 + 16 moles H * 1 + 4 moles oxygen * 16 + 1 mole aluminum * 27 + 3 moles chlorine * 35.5 + 3 moles sodium * 23 = 378

Approximate mass efficiency = 122/378 = 0.32

Chapter 7 Sample Homework Problem

1. The text noted that the atom and mass efficiencies for addition reactions are generally higher than for substitution or elimination reactions. To illustrate this concept, calculate the mass and atom efficiencies for the following reactions:

a.) (Addition reaction) Isobutylene + methanol→ methyl,tert-butyl ether
$C_4H_8 + CH_3OH \rightarrow (C_4H_9)\text{-}O\text{-}CH_3$

Calculate mass, carbon, hydrogen and oxygen efficiencies

b.) (Substitution reaction) Phenol + ammonia → aniline + water
$C_6H_5\text{-}OH + NH_3 \rightarrow C_6H_5\text{-}NH_2 + H_2O$

Calculate mass, carbon, hydrogen, nitrogen and oxygen efficiencies

c.) (Elimination reaction) Ethylbenzene → styrene + hydrogen
$C_6H_5\text{-}C_2H_5 \rightarrow C_6H_5\text{-}C_2H_3 + H_2$

Calculate mass, carbon, and hydrogen efficiencies

d.) Identify additional industrially significant examples of addition, substitution and elimination reactions; calculate atom and mass efficiencies for these reactions.

Chapter 8. Evaluating Environmental Performance During Process Synthesis

by

David T. Allen, David R. Shonnard, and Scott Prothero

The design of chemical processes proceeds through a series of steps, beginning with the specification of the input-output structure of the process and concluding with a fully specified flowsheet. Traditionally, environmental performance has only been evaluated at the final design stages, when the process is fully specified. This chapter presents methodologies that can be applied at a variety of stages in the design process, allowing the process engineer more flexibility in choosing design options that improve environmental performance.

The search for "greener chemistry", described in the previous chapter, can lead to many exciting developments. New, simpler synthesis pathways could be discovered for complex chemical products resulting in a process that generates less toxic byproducts and lowers the overall risk associated with the process. Toxic intermediates used in the synthesis of commodity chemicals might be eliminated. Benign solvents might replace more environmentally hazardous materials. However, these developments will involve new chemical processes as well as Green Chemistry.

The art and craft of creating chemical processes is the topic of a number of excellent textbooks (see, for example, Douglas, 1988). A fundamental theme that arises in each of these texts is that the design process proceeds through a series of steps each involving an evaluation of the associated environmental impacts. At the earliest stages of a design, only the most basic features of a process are proposed. These include the raw materials and chemical pathway to be used, as well as the overall material balances for the major products, by-products and raw materials. Large numbers of design alternatives are screened at this early design stage, and the screening tools used to evaluate the alternatives must be able to handle efficiently large numbers of alternative design concepts. As design concepts are screened, a select few might merit further study. Preliminary designs for the major pieces of equipment to be used in the process need to be specified for the design options that merit further study. Material flows for both major and minor by-products are estimated. Rough emission estimates, based on analogous processes, might be considered. At this development stage, where fewer design alternatives are considered, more effort can be expended in evaluating each design alternative, and more information is available to perform the evaluation. If a design alternative appears attractive at this stage, a small-scale pilot plant of the process might be constructed and a detailed process flow sheet for a full-scale process might be constructed. Very few new design ideas reach this stage, and the investments made in evaluating design alternatives at this level are substantial. Therefore, process evaluation and screening tools can be quite sophisticated.

Traditionally, evaluations of environmental performance have been restricted to the last stages of this engineering design process, when most of the critical design decisions have already been made. A better approach would be to evaluate environmental performance at each step in the design process. This would require, however, a hierarchy of tools for evaluating environmental performance. Tools that can be efficiently applied to large numbers of alternatives, using limited information, are necessary for evaluating environmental performance at the earliest design stages. More detailed tools could be employed at the development stages, where potential emissions and wastes have been identified. Finally, detailed environmental impact assessments would be performed as a process nears implementation.

This chapter and Chapter 11 present a hierarchy of tools for evaluating the environmental performance of chemical processes. Three tiers of environmental performance tools will be presented. The first tier of tools, presented in Section 8.2, is appropriate for situations where only chemical structures and the input -output structure of a process is known. Section 8.3 describes a second tier of tools, which is appropriate for evaluating the environmental performance of preliminary process designs. This tier includes tools for estimating wastes and emissions. Finally, Section 8.4 introduces methods for the detailed evaluation of flowsheet alternatives, which will be discussed in Chapter 11.

Chapter 8 Example Problem

Example 8.3-2

A company wants to sell a newly-developed substitute for dimethylsulfoxide (DMSO) in pharmaceutical manufacturing. 300,000 lb/yr of this new "drop-in" substitute for DMSO could be sold to two customer pharmaceutical plants who will each purchase the same volume of the substitute. US EPA requires submission of a Premanufacture Notice (PMN) for this new chemical. The PMN form requests estimated releases to all media from downstream customers (the pharmaceutical plants) in units of kg/day. Generate these estimates.

Solution

Assume that the physical/chemical properties of the new chemical match the properties of DMSO very closely. The customer plants are reluctant to divulge proprietary process information, but one detail they give is that the facilities operate five days each week for 50 weeks of the year. Based on a search of several release estimation resources you find that the US EPA document entitled "Compilation of Air Pollutant Emission Factors" (often referred to as "AP-42") contains emission factors for DMSO for the pharmaceutical industry. The reference table notes that these data are based on an industry survey. Because both the release-affecting properties and the industrial use of the new chemical and DMSO are so similar, you have concluded that these DMSO emission factors are suitable surrogates for estimating releases of your company's new chemical. The AP-42 DMSO emission factors for the pharmaceutical industry are 1% to air emissions, 28% to sewer, and 71% to incineration (AP-42, Section 6.13). You contacted the potential customers, and they acknowledged that these AP-42 emission factors reasonably represent their facilities.

Calculation: First calculate the amount used per day at each site, then apply the emission factors to calculate the release to the media.

1. Daily average amount (mass) used at each site =
   300,000 lb/yr / 2.20 kg/lb / 2 sites / (5 days/week x 50 weeks/yr) = 273 kg/day
2. Partition the daily use amount to the media based on the emission factors:
   release to air = 1% of 273 kg/day = 2.7 kg/day
   release to water = 28% of 273 kg/day = 76 kg/day
   release to incineration = 71% of 273 kg/day = 194 kg/day

Chapter 8 Sample Homework Problem

1. Compare the carbonylation of dinitrotoluene and the amine-phosgene routes for the production of toluene diisocyanate (TDI) using a Tier 1 economic and environmental performance evaluation. The amine- phosgene route involves the reaction of phosgene with toluenediamine in a chlorobenzene solvent. The carbonylation route has been demonstrated in laboratories, but is not presently a commercial technology. Data from the patent literature (see the Green Chemistry Expert System referenced in Chapter 7) indicate that the reaction of 2,4 dinitrotoluene with carbon monoxide occurs over a mixed oxide catalyst. Conversion approaches 100% with selectivity to the desired product ranging from 70 - 99%. Laboratory data indicate that the reaction can be performed in a chlorobenzene and pyridine solvent. Approximate stoichiometric data, based on the patent data, are given in the Table below. Compare the carbonylation of nitrobenzene and the amine phosgene routes for the production of methylene diphenylene diisocyanate (MDI).

Amine - phosgene route:

$$C_6H_3(CH_3)(NH_2)_2 + 2\ COCl_2 \Rightarrow C_6H_3(CH_3)(-N{=}C{=}O)_2 + 4\ HCl$$

Carbonylation of nitrobenzene:

$$C_6H_3(CH_3)(NO_2)_2 + 6\ CO \Rightarrow C_6H_3(CH_3)(-N{=}C{=}O)_2 + 4\ CO_2$$

Compound	*Pounds produced or pounds of raw material required per pound of MDI**	*Cost ($/lb)***	*PEL ($\mu g/m^3$)*	*Overall inhalation toxicity factor*	*Overall oral toxicity factor*
Amine - phosgene route					
toluene diamine	-0.76	0.576	0.1 (est.)	NA	NA
chlorobenzene	-0.01	0.550	350	100	100
hydrochloric acid	0.4 (est.)	0.027	7	100	100
phosgene	-1.26	0.610	0.4	NA	NA
TDI	1.00	1.340	0.14	100,000	100

Carbonylation route					
dinitrotoluene	1.04 (est.)	0.365	1.5	1,000	1,000
carbon monoxide	1.0 (est.)	0.040	55	NA	NA
TDI	1.00	1.340	0.14	100,000	100
carbon dioxide	1.0 (est.)	-	9000	NA	NA

* A negative stoichiometric index indicates that a material is consumed; a positive index indicates that it is produced in the reaction

**Chang, 1996

Chapter 9. Unit Operations and Pollution Prevention

by
David R. Shonnard

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'*.

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

$$t = 0.882\,\frac{n^{3/4}\, L_f^{3/4}}{u'^{7/4}} = 0.882\,\frac{(1.16\times10^{-5})^{3/4}(0.5)^{3/4}}{(2.36)^{7/4}} = 2.32\times10^{-5}\ \text{sec}$$

$(k_1 B_o t)(A_o / B_o) = (k_1 t A_o) = (35)(2.32\times10^{-5})(0.2) = 1.62\times10^{-4}$ 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).

Chapter 10. Flowsheet Analysis for Pollution Prevention

by
Kirsten Sinclair Rosselot and David T. Allen

The environmental performance of a process flowsheet depends on both the performance of the individual unit operations that make up the flowsheet and on the level to which the process streams have been networked and integrated. While Chapter 9 describes methods for improving the performance of individual operations, this chapter examines methods for assessing and improving the degree to which the unit operations are integrated. Specifically, Section 10.2 examines process energy integration and Section 10.3 examines process mass integration. The methods presented in these sections, and the case study presented in Section 10.4, will demonstrate that improved process integration can lead to improvements in overall mass and energy efficiency.

Before examining process integration in detail, however, it is useful to review the methods that exist for systematically assessing and improving the environmental performance of process designs. A number of such methods are available. Some are analogous to Hazard and Operability (HAZ-OP) Analyses (e.g., see Crowl and Louvar, 1990).

Section 9.7 briefly describes how a HAZ-OP analysis is performed; to summarize, the potential hazard associated with each process stream is evaluated qualitatively (and sometimes quantitatively) by systematically considering possible deviations in the stream. Table 10.1-1 gives the guidewords and examples of deviations used in HAZ-OP analysis. Each guide word is applied to each relevant stream characteristic, the possible causes of the deviation are listed, and the consequences of the deviation are determined. Finally, the action(s) required to prevent the occurrence of the deviation are determined.

Table 10.1-1 Guide Words and Deviations in HAZ-OP Analysis.

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.

For a single pipeline taking fluid from one storage tank to another, there may be several possible deviations, such as:

- no flow
- more flow
- more pressure
- more temperature

- less flow
- less temperature
- high concentration of a particular component
- presence of undesirable compounds

Note that each deviation may have more than one possible cause so that this set of deviations would be associated with dozens of possible causes. It would be difficult to consider all the deviations and their consequences without a structured system for analyzing the flowsheet. A similar analysis framework has been employed, in a series of case studies, to identify environmental improvements in process flowsheets (DuPont, 1993). In these case studies, a series of systematic questions are raised concerning each process stream or group of unit processes. Typical questions include:

- What changes in operating procedures might reduce wastes?
- Would changes in raw materials or process chemistry be effective?
- Would improvements in process control be effective?

Process alternatives, such as those defined in Chapter 9, can be identified, and in this way the environmental improvement opportunities for the entire flowsheet can be systematically examined. (See, for example the cases from the DuPont report described by Allen and Rosselot,1997).

Other methods for systematically examining environmental improvement opportunities for flowsheets have been developed based on the hierarchical design methodologies developed by Douglas (1992). The hierarchical levels are shown in Table 10.1-2. Note that Level 1 in this table applies only to processes that are being designed, not to existing processes. The hierarchy is organized so that decisions that affect waste and emission generation at each level limit the decisions in the levels below it.

As an example of the use of hierarchical analysis procedures, consider a case study drawn from the AMOCO/US EPA Pollution Prevention Project at AMOCO's refinery in Yorktown, Virginia (Rossiter and Klee, 1995). In this example, the flowsheet of a fluidized-bed catalytic cracking unit (FCCU) is evaluated for pollution prevention options. A flowsheet of the unit is shown in Figure 10.1-1.

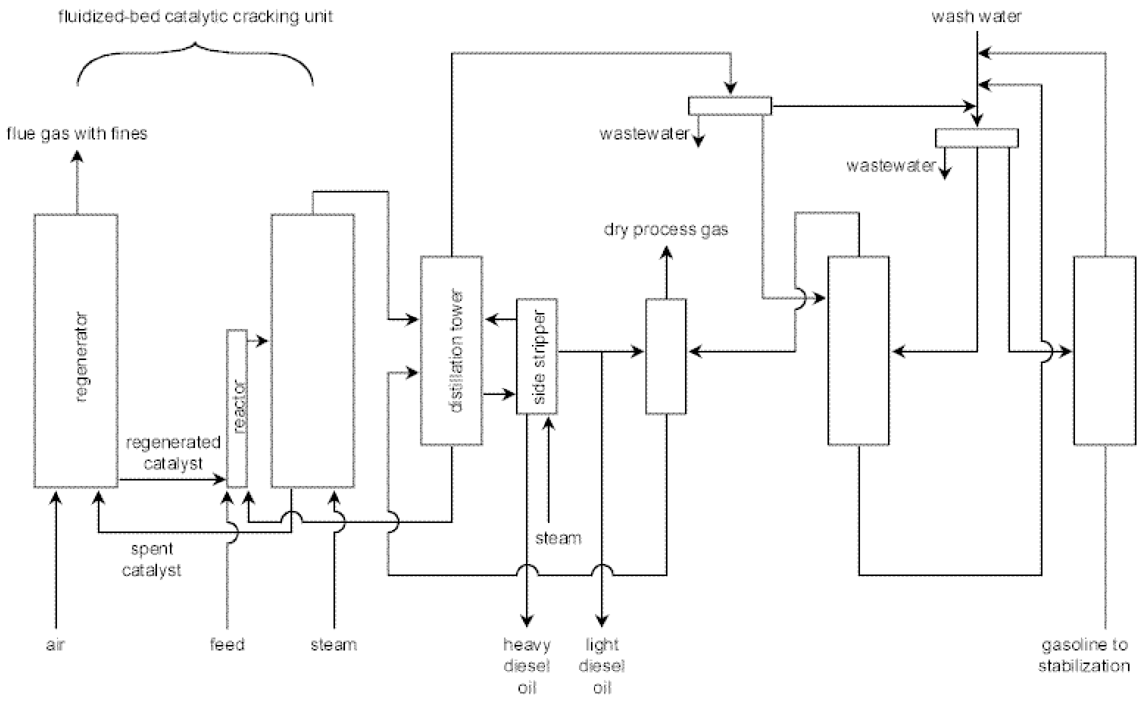


Figure 10.1-1 Process flow diagram of a fluidized-bed catalytic cracking unit.

Beginning with Level 2 of the hierarchy listed in Table 10.1-2, (input-output structure), the following pollution prevention strategies were generated:

1) Improve quality of the feed to eliminate or reduce the need for the vapor line washing system shown in the upper right-hand corner of Figure 10.1-1.

2) Reduce steam consumption in the reactor so that there is less condensate to remove from the distillation system.

3) Within the catalyst regeneration system, the loss of fines (upper left hand corner of Figure 10.1-1) is partly a function of the air input rate. A reduction in air flow (e.g. by using oxygen enrichment) is a possible means of reducing the discharge of fines.

Two ideas were generated during review of the recycle structure (level 3):

1) The reactor uses 26,000 lb/hr of steam. This is provided from the utility steam system. If this could be replaced with steam generated from process water, the liquid effluent from the unit would be reduced. Volatile hydrocarbons contained in the recycled steam would be returned directly to the process. Catalyst regeneration consumes more than 11,000 lb/hr of steam. It may be possible to satisfy this duty with "dirty steam" as well, since the hydrocarbon content would be incinerated with the coke in the regenerator.

2) Used wash water is collected at several points and then purged from the process. If it could be recovered and recycled instead, or if recycled water from other sources could be used for washing in place of fresh water, fresh water usage and wastewater generation could both be reduced by about 10,500 lb/hr.

Table 10.1-2 Levels for Hierarchical Analysis for Pollution Prevention (Adapted from Douglas, 1992)

Design Levels
1. Identify the material to be manufactured
2. Specify the input/output structure of the flowsheet
3. Design the recycle structure of the flowsheet
4. Specify the separation system
4a. General structure: phase splits
4b. Vapor recovery system
4c. Liquid recovery system
4d. Solid recovery system
5. Process integration
5a. Integrate process heating and cooling demands
5b. Identify process waste recycling and water reuse opportunities

Three options were identified for separation systems (level 4):

1) Replace heating done by direct contacting with steam by heating with reboilers.

2) Place additional oil-water separators downstream of existing condensate collection points and recover hydrocarbons.

3) Improve gas-solid separation downstream of the regenerator to eliminate loss of catalyst fines. This might simply require better cyclone and/or ductwork design, or electrostatic precipitation.

These first four levels of the design hierarchy lead us to the types of process improvements described in Chapter 9—improvements in the reactor and improvements in the separation system. As Table 10.2-1 notes, the next step in the design process is to identify opportunities for process integration. This is the main topic of this chapter and the next several sections describe methods for process energy integration and methods for identifying process waste recycling and reuse opportunities.

Chapter 10 Example Problem

Example 10.4 Constructing a Composition Interval Diagram

Construct a CID for the rich streams of Table 10.8. With the aid of this CID, calculate the mass transferred out of the rich streams in units of kg/s within each region of the CID. The mass transferred from the rich streams within each region is equal to $(y^{out}-y^{in})\times\Sigma R_i$, where y^{out} and y^{in} are the exiting and entering rich stream mass fractions, respectively, and ΣR_i is the sum of the rich stream flow rates in the region. Note that mass transfer is negative for the rich streams because they are losing mass.

Table 10.8 Stream data for three rich streams and one lean stream

Rich Stream				Lean Stream			
Stream	Flow Rate, kg/s	y^{in}	y^{out}	Stream	Flow Rate, kg/s	x^{in}	x^{out}
R_1	5	0.10	0.03	L	15	0.00	0.14
R_2	10	0.07	0.03				
R_3	5	0.08	0.01				

Solution

The rich streams are mapped from Table 10.8 to generate the CID shown in Figure 10.20. The mass transferred in each region is:

region 1= $(y^{out}-y^{in})\times\Sigma R_i$ = (0.08-0.10)5 kg/s = -0.10 kg/s
region 2= (0.07-0.08)(5+5) kg/s = -0.10 kg/s
region 3= (0.03-0.07)(5+10+5) kg/s = -0.80 kg/s
region 4= (0.01-0.03)5 kg/s = -0.10 kg/s

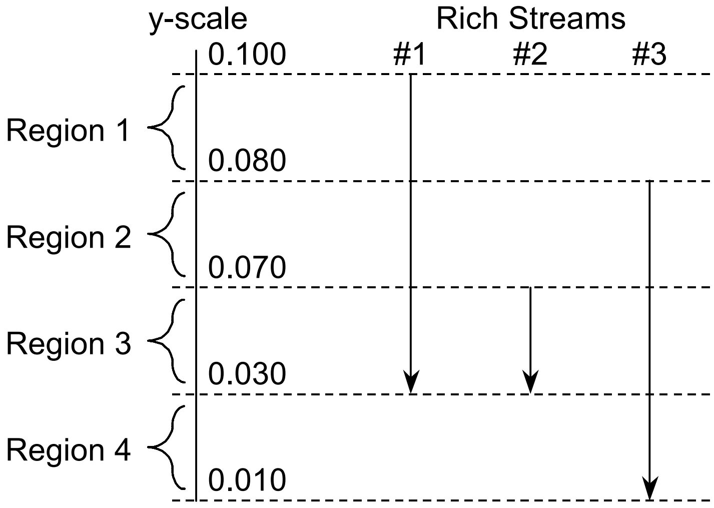


Figure 10.20 Composition interval diagram for the rich streams of Table 10.8

In Figure 10.19, the compositions of the rich and lean streams are on separate axes. These axes can be combined by applying the equilibrium relationship. If the equilibrium relationship in the region of interest for the species considered in this problem is given by

$$y = 0.67x^*,$$

then a mass fraction of $y = 0.1$ in the rich stream is in equilibrium with a mass fraction of $x^* = 0.15$ in the lean stream. By converting the lean stream compositions of Figure 10.19 to the rich stream compositions with which they are in equilibrium, and vice versa, a combined CID with shared axes as shown in Figure 10.21 can be constructed.

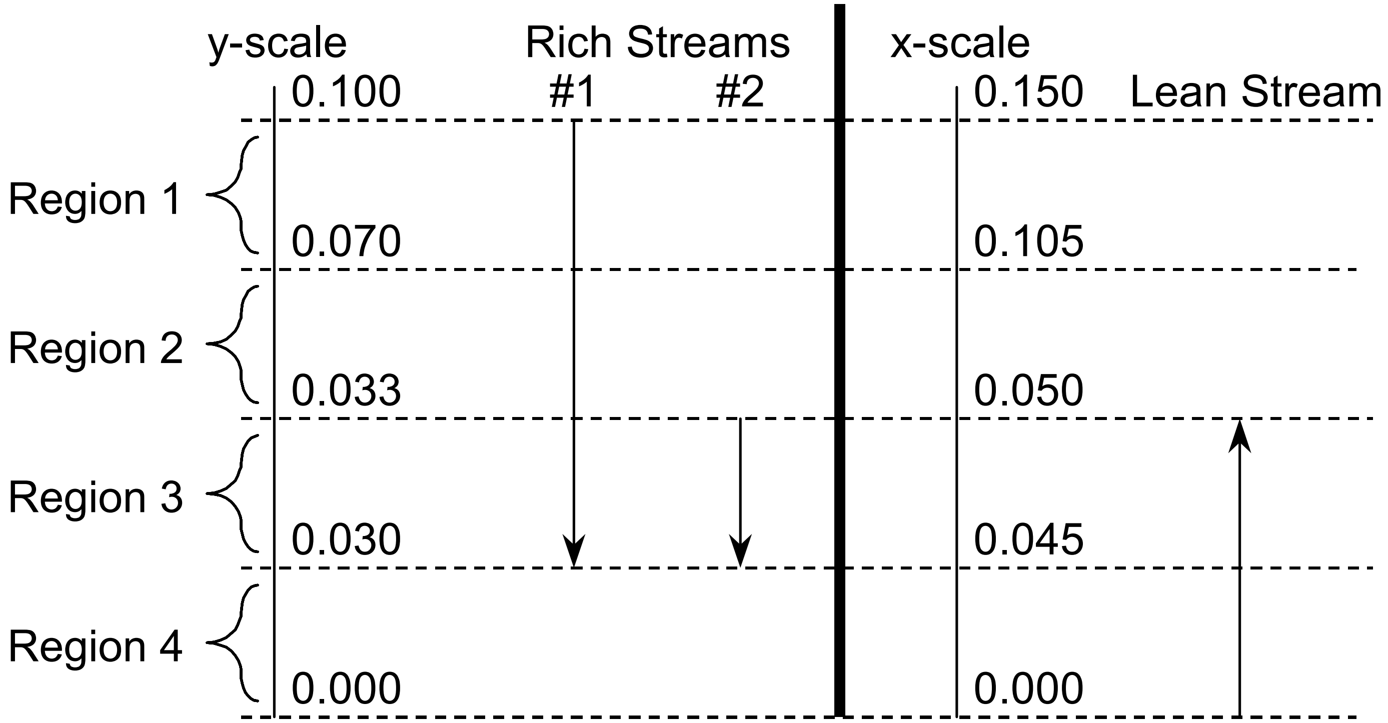


Figure 10-21. Combined composition interval diagram for the streams of Table 10.7.

Chapter 10 Sample Homework problem

1. Determine the amount of energy savings that could be achieved by putting in place a Heat exchange network in the hot water system for a typical house.

a.) Begin by identifying the hot water streams from which heat can be extracted (e.g., dishwasher effluent, shower effluent). For each of these streams, estimate a water exit temperature and a daily flow rate.

b.) Assume that these hot streams will be contacted with the cold supply water entering the hot water heater and estimate the amount of energy that could be extracted from the hot streams. Determine the annual energy savings if the home uses an electric hot water heater and electricity costs $0.06/kwh. Make reasonable assumptions about the efficiency of the hot water heater (fraction of the electricity that goes into heated water used by the homeowner).

c.) The cost of an installed, non-contact, single tube, shell and tube exchanger for this application is approximately $500. Assume that the hot water exit lines already pass near the water heater so that little additional plumbing is required. Determine the time required to repay the installation cost using money saved in energy costs.

Chapter 11. Evaluating the Environmental Performance of a Flowsheet

by
David R. Shonnard

After the process flowsheet has been established and energy and mass efficiency measures have been applied (Chapter 10), it is appropriate for a detailed environmental impact evaluation to be performed. The end result of the impact evaluation will be a set of environmental metrics (indices), which represent the major environmental impacts, or risks of the entire process. A number of indexes are needed to account for potential damage to human health and to several important environmental media. The indexes can be used to determine the potential impact to human health and the environment. The indices can be used in several important engineering applications during process design, including the ranking of technology selection, the optimizing of in-process waste recycle/recovery processes, and the evaluation of the modes of reactor operation.

In a quantitative risk assessment, it is shown that impacts are a function of dose that dose is a function of concentration, and that concentration is a function of emission rate. Therefore, emissions from a process design flowsheet are the primary piece of information required for impact assessment. The concentrations in the relevant compartments of the environment (air, water, and soil) are dependent upon the emissions and the location and chemical and physical properties of the pollutants. A suitable fate and transport model can transform the emissions into environmental concentrations. Finally, information regarding toxicity or inherent impact is required to convert the concentration-dependant doses into probabilities or harm (risk). Based on this understanding of risk assessment, the steps for environmental impact assessment are grouped into three categories, a) estimates of the rates of release for all chemicals in the process, b) calculation of environmental fate and transport and environmental concentrations, and c) the accounting for multiple measures of risk using toxicology and inherent environmental impact information.

Ideally, one would prefer to conduct a *quantitative risk assessment* when comparing environmental performance of chemical process designs. Although this approach is preferred when the source and receptor are well defined and localized, it is not well suited for industrial releases that often affect not only local, but also regional and global environments. Also, the computing resources needed to perform a quantitative risk assessment for all release sources and receptors would tax the abilities of even the largest chemical manufacturer. A more achievable approach is to abandon quantitative risk assessment in preference to the assessment of potential environmental and health risks. The establishment of the potential impacts of chemical releases is sufficient for comparing the environmental risks of chemical process designs. In this chapter, material is presented which establish methodologies for assessing the potential for environmental impacts of chemical processes and their designs.

In this development, we will utilize the concept of *benchmarking*. First introduced for the assessment of global warming and ozone depletion potentials of refrigerants in the early 1990's, benchmarking takes the ratio of the environmental impact of a chemical's release to the impact of the identical release of a well-studied compound. A value greater than 1 for this dimensionless quantity indicates that the chemical has a greater potential for environmental impact than the benchmark compound. The product of the benchmarked environmental impact potential with the process emission rate results in the equivalent emission of the benchmark compound in terms of environmental impact. In this text, we adopt the benchmarking concept when assessing the environmental and toxicological impact potentials of releases from chemical processes. (Heijungs et. al. 1992)

Section 11.2 is a description of a multimedia compartment model approach for determining fate and transport of chemical releases into the environment. This model predicts the long-time and large-spatial scale distribution of chemicals using multiple compartments as the physical structure for the environment. Section 11.3 is a presentation of a Tier 3 environmental assessment (Tier 1 and Tier 2 assessments are discussed in Chapter 8) consistent with the goal of efficiently comparing chemical process designs.

Chapter 11 Example Problem

Example Problem 11.2 Global Warming Index for Air Emissions of 1,1,1-Trichloroethane from a Production Process

1,1,1-Trichloroethane (TCA) is used as an industrial solvent for metal cleaning, as a reaction intermediate, and for other uses (U.S. EPA, 1979-1991)). A major processing route for TCA is by hydrochlorination of vinyl chloride in the presence of a $FeCl_3$ catalyst to produce11,1-dichloroethane, followed by chlorination of this intermediate. Sources for air emissions include distillation condenser vents, storage tanks, handling and transfer operations, fugitive sources, and secondary emissions from wastewater treatment. We wish to estimate the global warming impact of the air emissions from this process. Include direct impacts to the environment (from 1,1,1-TCA) and indirect impacts from energy usage (CO_2 and NOx release) in your analysis. Data below show the major chemicals which impact global warming when emitted from the process.

Determine the global warming index for the process and the percentage contribution for each chemical.

Data: Air Emissions (15,500 kg 1,1,1-TCA/hr Process)

Chemical	m_i (kg/hr)	GWP
TCA	40.5	100
CO_2	7,760	1
NOx	93	40

TCA emission rate estimated using EPA factors (U.S. EPA, 1979-1991). CO_2 and NOx emission rates estimated from a Life Cycle Assessment of Ethylene Production (Allen and Rosselot, 1997; Boustead, 1993).

<u>Solution</u>:
Using equation (11.3-4), the process global warming index is

$$
\begin{aligned}
I_{GW} &= (40.5\ \text{kg/hr})(100) + (7{,}760\ \text{kg/hr})(1) + (93\ \text{kg/hr})(40) \\
&= 4{,}050 + 7{,}760 + 3{,}720 \\
&\boxed{= 15{,}530\ \text{kg/hr}}
\end{aligned}
$$

The percent of the process I_{GW} for each chemical is;
1,1,1-TCA ; (4,050/15,530)x100 = 26.08%
CO_2 ; (7,760/15,530)x100 = 49.97%
NOx ; (3,720/15,530)x100 = 23.95%

<u>Discussion</u>: This case study demonstrates that the majority of the global warming impact from the production of 1,1,1-TCA is from the energy requirement of the process and not from the emission of the chemical with the highest global warming potential. This analysis assumes that fossil fuels were used to satisfy the energy requirements of the process. If renewable resources were used (biomass based fuels), the impact of CO_2 to the global warming would be significantly reduced. The majority of the global warming impact of 1,1,1-TCA will likely be felt during the usage stage of its life cycle, not the production stage. A complete Life Cycle Assessment of 1,1,1-TCA will be necessary to demonstrate this.

Chapter 11 Sample Homework Problem

1. As a requirement of the 1990 Clean Air Act Amendments, automobile fuels sold in urban areas must be reformulated gasoline, also known as RFG. RFG must contain a certain level of oxygenates (such as MTBE, ETBE, TAME, or ethanol). The maximum incremental reactivities (MIR) values for ethanol and other potential octane boosters are provided below.

Ethanol	1.34
Toluene	2.70
Xylenes	7.10
Base Fuel	1.5

Calculate by what percentage the ozone producing potential of an ethanol fuel blend (10% ethanol, 90% base fuel) is reduced compared to a fuel blend containing 10% of toluene and 90% base fuel and another blend containing 10% xylenes and 90% base fuel, respectively. Use the provided MIR values for this calculation.

Chapter 12. Environmental Cost Accounting

by
Kirsten Sinclair Rosselot and David T. Allen

Costs associated with poor environmental performance can be devastating. Waste disposal fees, permitting costs, and liability costs can all be substantial. Wasted raw material, wasted energy and reduced manufacturing throughput are also consequences of wastes and emissions. Corporate image and relationships with worker and communities can suffer if environmental performance is substandard. But, how can these costs be quantified?

This chapter will review the tools available for estimating environmental costs. Many of these tools are still in their developmental stages, and practices therefore vary widely from company to company. In general, however, accounting practices have acted as a barrier to implementation of green engineering projects because they hide the costs of poor environmental performance. Many companies are now giving more consideration to all significant sources of environmental costs. The principle is that if costs are properly accounted for, business management practices that foster good economic performance will also foster superior environmental performance.

The relationships between economic and environmental performance are examined in a number of steps. First, in Section 12.2, a few key terms are defined to simplify and clarify the presentation of material. In Section 12.3, the magnitude and types of environmental costs typically encountered by companies are reviewed. Then, in Section 12.4, a framework for assessing environmental costs is described. Finally, sections 12.5 through 12.8 describe specific methods for evaluating environmental costs.

Prerequisites to fully understanding the benefits of environmental accounting practices are an understanding of the time value of money and some familiarity with present value, payback period, internal rate of return, and other financial evaluation calcuations. These concepts are covered in textbooks on engineering economics (see, for example, Valle-Riestra, 1983). Also, it is assumed that the reader understands how to evaluate potential environmental impacts associated with products and processes (see Chapter 11).

Chapter 12 Example Problem
Example 12-2

A chemical manufacturing facility buys raw material for $0.50 per pound and produces 90 million pounds per year of product, which is sold for $0.75 per pound. The process is typically run at 90% selectivity and the raw material that is not converted into product is disposed of at a cost of $0.80 per pound (by incineration). A process improvement allows the process to be run at 95% selectivity, allowing the facility to produce 95 million pounds per year of product. What is the net revenue of the facility (product sales - raw material costs - waste disposal costs) before and after the change? How much of the increased net revenue is due to increased sales of product and how much is due to decreased waste disposal costs?

Solution

The net revenue before the change is:

(90 million pounds * $0.75/pound - 100 million pounds raw material *$0.50/pound - 10 million pounds waste * $0.80) = $9.5 million/year

The net revenue after the change is:

(95 million pounds * $0.75/pound - 100 million pounds raw material *$0.50/pound - 5million pounds waste * $0.80) = $17.25 million/year

Of the difference ($7.75 million), about half ($3.75 million) is due to increased product sales and the remainder is due to decreased disposal cost. Note that the disposal cost assumed in this example is very high and thus represents a likely upper bound on these costs. It should also be noted that the cost of capital depreciation, per pound of product is reduced after the change.

Chapter 12 Sample Homework Problems

1. Lurmann, et al. (1999) have estimated the costs associated with ozone and fine particulate matter concentrations above the National Ambient Air Quality Standards (NAAQSs) in Houston. They estimated that the economic impacts of early mortality and morbidity associated with elevated fine particulate matter concentrations (above the NAAQS) are approximately $3 billion/year. Hall, et al. (1992), performed a similar assessment for Los Angeles. In the Houston study, Lurmann et al examined the exposures and health costs associated with a variety of emission scenarios. One set of calculations demonstrated that a decrease of approximately 300 tons/day of fine particulate matter emissions resulted in a 7 million person-day decrease in exposure to particulate matter concentrations above the proposed NAAQS for fine particulate matter, 17 less early deaths per year, and 24 fewer cases of chronic bronchitis per year. Using estimated costs of $300,000 per case of chronic bronchitis and $6,000,000 per early death, estimate the social cost per ton of fine particulate matter emitted. How does this compare to the range of values quoted by the AIChE CWRT? Review the procedures for estimating costs (see Hall, et al., 1992) and comment on the uncertainties associated with the methodology.

Chapter 13. Life-Cycle Concepts, Product Stewardship and Green Engineering

by
Kirsten Rosselot and David T. Allen

Products, services, and processes all have a life cycle. For products, the life cycle begins when raw materials are extracted or harvested. Raw materials then go through a number of manufacturing steps until the product is delivered to a customer. The product is used, then disposed of or recycled. These product life-cycle stages are illustrated in Figure 13.1-1, along the horizontal axis. As shown in the figure, energy is consumed and wastes and emissions are generated in all of these life-cycle stages.

Processes also have a lifecycle. The life cycle begins with planning, research and development. The products and processes are then designed and constructed. A process will have an active lifetime, then will be decommissioned and, if necessary, remediation and restoration may occur. Figure 13.1-1, along its vertical axis, illustrates the main elements of this process life cycle. Again, energy consumption, wastes and emissions are associated with each step in the life cycle.

Traditionally, product and process designers have been concerned primarily with product life-cycle stages up to manufacturing. That focus is changing. Increasingly, chemical product designers must consider how their products will be recycled. They must consider how their consumers use their products. Process designers must avoid contamination of the sites at which their processes are located. Simply stated, design engineers must become stewards for their products and processes throughout their life cycles. These increased responsibilities for products and processes throughout their life cycles have been recognized by a number of professional organizations. Table 13.1-1 describes a Code of Product Stewardship developed by the Chemical Manufacturers' Association (now named the American Chemistry Council).

Effective product and process stewardship requires designs that optimize performance throughout the entire life cycle. This chapter provides an introduction to tools available for assessing the environmental performance of products and processes throughout their life cycle. The primary focus is on product life cycles, but similar concepts and tools could be applied to process life cycles. Sections 13.2 and 13.3 present quantitative tools used in product life cycles assessments (LCAs). Section 13.4 presents more qualitative tools. Section 13.5 describes a number of applications for these tools and Section 13.6 summarizes the main points of the chapter.

Table 13.1-1 The Chemical Manufacturers' Association (American Chemistry Council) Product Stewardship Code

The purpose of the Product Stewardship Code of Management Practices is to make health, safety and environmental protection an integral part of designing, manufacturing, marketing, distributing, using, recycling and disposing of our products. The Code provides guidance as well as a means to measure continuous improvement in the practice of product stewardship.

The scope of the Code covers all stages of a product's life. Successful implementation is a shared responsibility. Everyone involved with the product has responsibilities to address society's interest in a healthy environment and in products that can be used safely. All employers are responsible for providing a safe workplace, and all who use and handle products must follow safe and environmentally sound practices.

The Code recognizes that each company must exercise independent judgment and discretion to successfully apply the Code to its products, customers and business.

Relationship to Guiding Principles

Implementation of the Code promotes achievement of several of the Responsible Care Guiding Principles:

- ♦ To make health, safety and environmental considerations a priority in our planning for all existing and new products and processes;
- ♦ To develop and produce chemicals that can be manufactured, transported, used and disposed of safely;
- ♦ To extend knowledge by conducting or supporting research on the health, safety and environmental effects of our products, processes and waste materials;
- ♦ To counsel customers on the safe use, transportation and disposal of chemical products;
- ♦ To report promptly to officials, employees, customers and the public, information on chemical related health or environmental hazards and to recommend protective measures;
- ♦ To promote the principles and practices of Responsible Care by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of chemicals.

Figure 13.1-1 Product life cycles include raw material extraction, material processing, use and disposal steps, and are illustrated along the horizontal axis. Process life cycles include planning, research, design, operation and decommissioning steps and are shown along the vertical axis. In both product and process life cycles, energy and materials are used at each stage of the life cycle and emissions and wastes are created.

(Insert Figure here)

Chapter 13 Sample Example Problem

Example 13.2 Selected environmental indices from the Environmental Priority Strategies system.

In the EPS system, environmental indices are multiplied by the appropriate quantity of raw materials used or emissions released to arrive at Environmental Load Units (ELUs), which can then be added together to arrive at an overall ELU for the subject of the life-cycle study. Table 13.8 gives selected environmental weighting factors from the EPS system. Calculate the environmental load units due to air emissions from one kilogram of ethylene production. Emissions are 0.53 kg, 0.006 kg, 0.0009 kg, and 0.009 kg of carbon dioxide, nitrogen oxides, carbon monoxide, and sulfur oxides, respectively (Boustead, 1993).

Solution

Total ELUs due to air emissions are

$$\begin{gathered} 0.53 \text{ kg } CO_2 \times 0.09 \text{ ELU/kg } CO_2 \\ 0.006 \text{ kg } NO_x \times 0.22 \text{ ELU/kg } NO_x \\ 0.0009 \text{ kg CO} \times 0.27 \text{ ELU/kg CO} \\ 0.009 \text{ kg } SO_x \times 0.10 \text{ ELU/kg } SO_x \\ = 0.05 \text{ ELU.} \end{gathered}$$

Note that if quantities of raw materials or water emissions were given, the ELUs for these inputs would be added to the ELUs for the air emissions.

Chapter 13 Sample Homework Problem

1. (From Allen, et al., 1992) At the supermarket checkstand, customers are asked to choose whether their purchases should be placed in unbleached paper grocery sacks or in polyethylene grocery sacks. Some consumers make their choice based on the perception of the relative environmental impacts of these two products. This problem will quantitatively examine life cycle inventory data on the energy use and air emissions for these two products.

Life cycle inventories for paper and polyethylene grocery sacks have resulted in the data given below, and these data will be used in comparing the two products. Assume that the functional unit to be used in this comparison is a defined volume of groceries to be transported, and that based on this functional unit, 2 plastic sacks are equivalent to one paper sack.

Air Emissions and Energy Requirements for Paper and Polyethylene Grocery Sacks (Allen, et al., 1992)

Life-cycle Stages	Paper sack air emissions (oz/sack)	Plastic sack air emissions (oz/sack)	Paper sack air energy req'd (Btu/sack)	Plastic sack air energy req'd (Btu/sack)
Materials manufacture plus product manufacture plus product use	0.0516	0.0146	905	464
Raw materials acquisition plus product disposal	0.0510	0.0045	724	185

Note: These data are based on past practices and may not be current.

a.) Using the data in the Table, determine the amount of energy required and the quantity of air pollutants released per plastic sack. Also determine the amount of energy required and the quantity of air pollutants released for the quantity of paper sacks capable of carrying the same volume of groceries as the plastic sack. Both the air emissions and the energy requirements are functions of the recycle rate, so perform your calculations at three recycle rates: 0%, 50% and 100% recycled. Note that a 50% recycle rate indicates that half of the sacks are disposed of and the other half are recycled after the product use stage of their life cycle.

b.) Plot the energy requirements calculated in Part a.) as a function of the recycle rate for both sacks. Do the same for the air emissions. Compare the energy requirements and air emissions of the sacks at different recycle rates.

c.) Discuss the relative environmental impacts of the two products. Do the results allow for a comprehensive comparison?

d.) The material and energy requirements of the plastic sacks are primarily derived from petroleum, a non-renewable resource. In contrast, the paper sacks rely on petroleum to only a limited extent and only for generating a small fraction of the manufacturing and transportation energy requirements. Compare the amount of petroleum required for the manufacture of two polyethylene sacks to the amount of energy necessary to provide 10% of the energy required in the manufacture of one paper sack. Assume 0% recycle and that 1.2 lb of petroleum is required to manufacture 1 lb of polyethylene. The higher heating value of petroleum is 20,000 BTU/lb.

e.) In this problem, we have assumed that 2 plastic sacks are equivalent to one paper sack. Does the uncertainty in the equivalency between paper and plastic sacks affect any of your conclusions?

Chapter 14. Industrial Ecology

by
David T. Allen

The environmental performance of chemical processes is governed not only by the design of the process, but also by how the process integrates with other processes and material flows. Consider a classic example - the manufacture of vinyl chloride.

Billions of pounds of vinyl chloride are produced annually. Approximately half of this production occurs through the direct chlorination of ethylene. Ethylene reacts with molecular chlorine to produce ethylene dichloride (EDC). The EDC is then pyrolyzed, producing vinyl chloride and hydrochloric acid.

$$Cl_2 + H_2C{=}CH_2 \Rightarrow Cl\,H_2C\text{-}CH_2\,Cl$$

$$Cl\,H_2C\text{-}CH_2\,Cl \Rightarrow H_2C{=}CH\,Cl + HCl$$

In this synthesis route, one mole of hydrochloric acid is produced for every mole of vinyl chloride. Considered in isolation, this process might be considered wasteful. Half of the original chlorine winds up, not in the desired product, but in a waste acid. But the process is not operated in isolation. The waste hydrochloric acid from the direct chlorination of ethylene can be used as a raw material in the oxychlorination of ethylene. In this process, hydrochloric acid, ethylene and oxygen are used to manufacture vinyl chloride.

$$HCl + H_2C{=}CH_2 + 0.5\ O_2 \Rightarrow H_2C{=}CH\,Cl + H_2O$$

By operating both the oxychlorination pathway and the direct chlorination pathway, as shown in Figure 14.1 -1, the waste hydrochloric acid can be used as a raw material and essentially all of the molecular chlorine originally reacted with ethylene is incorporated into vinyl chloride. The two processes operate synergistically and an efficient design for the manufacture of vinyl chloride involves both processes.

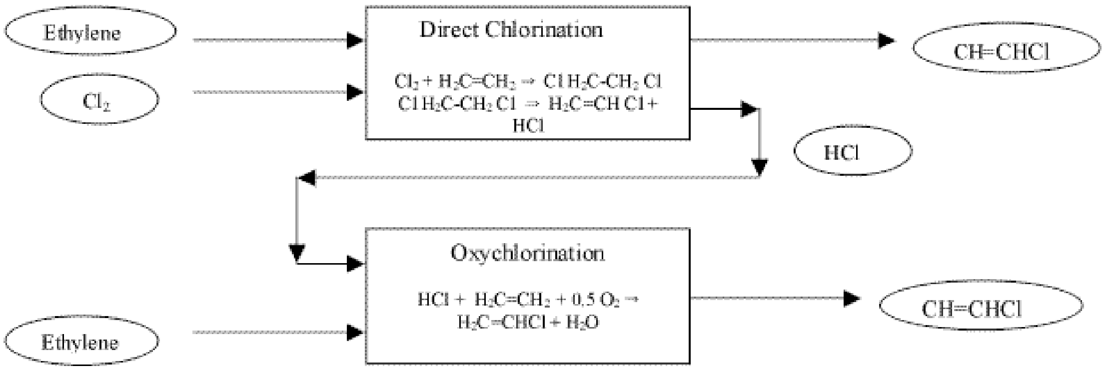


Figure 14.1 -1 Byproduct hydrochloric acid from the direct chlorination of ethylene is used as a raw material in the oxychlorination process; by operating the two processes in tandem, chlorine is used efficiently.

Additional efficiencies in the use of chlorine can be obtained by expanding the number of processes included in the network. In the network involving direct chlorination and oxychlorination processes, both processes incorporate chlorine into the final product. Recently, more extensive chlorine networks have emerged linking several isocyanate producers into vinyl chloride manufacturing networks (McCoy, 1998). In isocyanate manufacturing, chlorine is reacted with carbon monoxide to produce phosgene:

$$CO + Cl_2 \qquad COCl_2$$

The phosgene is then reacted with an amine to produce an isocyanate and byproduct hydrochloric acid:

$$RNH_2 + COCl_2 \qquad RNCO + 2\ HCl$$

The isocyanate is subsequently used in urethane production, and the hydrochloric acid is recycled. The key feature of the isocyanate process chemistry is that chlorine does not appear in the final product. Thus, chlorine can be processed through the system without being consumed. It may be transformed from molecular chlorine to hydrochloric acid, but the chlorine is still available for incorporation into final products, such as vinyl chloride, that contain chlorine. A chlorine-hydrogen chloride network incorporating both isocyanate and vinyl chloride has developed in the Gulf Coast of the United States. The network is shown in Figure 14.1-2. Molecular chlorine is manufactured by Pioneer and Vulcan Mitsui. The molecular chlorine is sent to both direct chlorination processes and to isocyanate manufacturing. The byproduct hydrochloric acid is sent to oxychlorination processes or calcium chloride manufacturing. The network has redundancy in chlorine flows, such that most processes could rely on either molecular chlorine or hydrogen chloride.

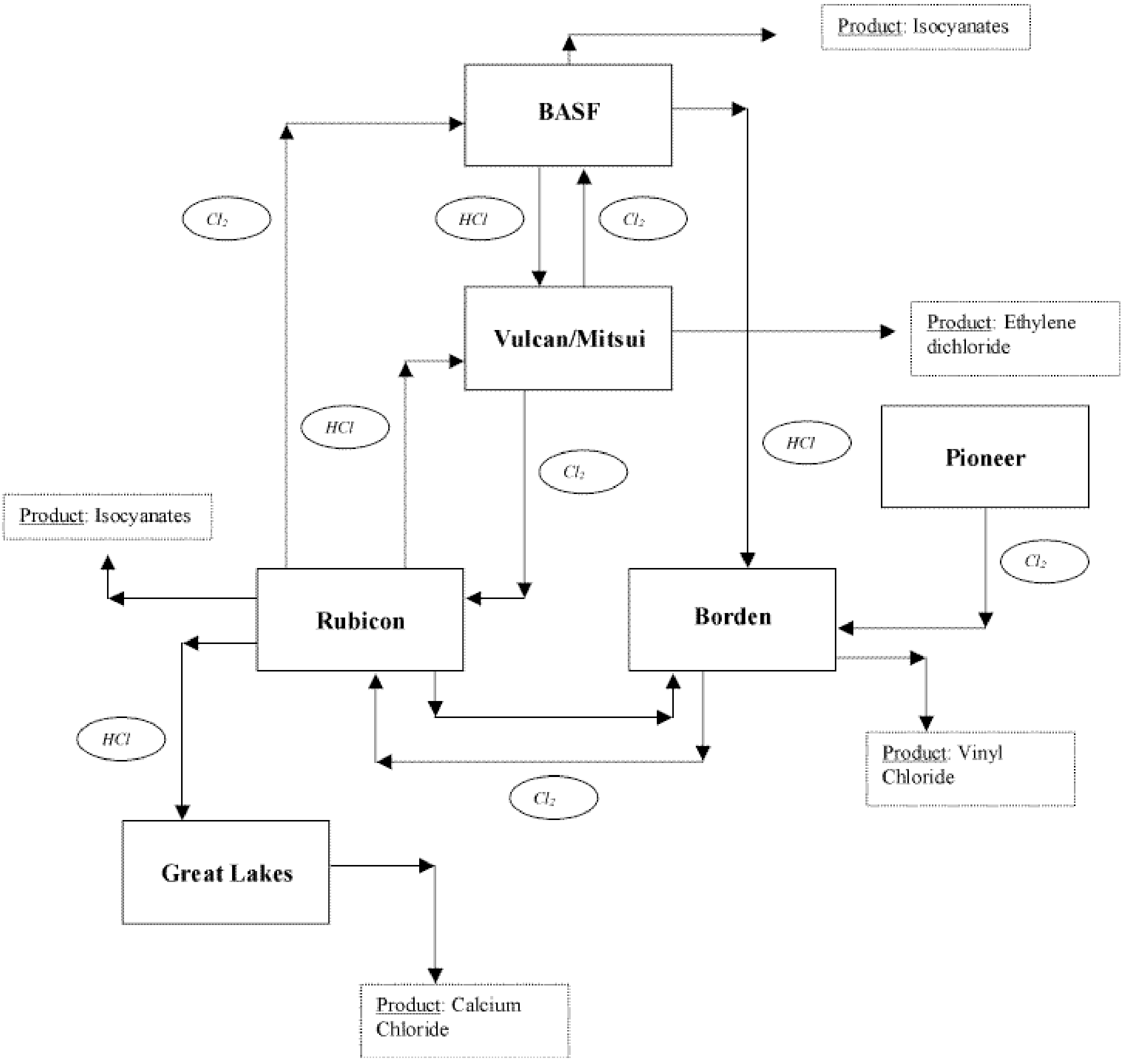


Figure 14.1-2 Chlorine flows in combined vinyl chloride and isocyanate manufacturing.

Consider the advantages of this network to the various companies (Francis, 2000).

- Vulcan/Mitsui effectively rents chlorine to BASF and Rubicon for their isocyanate manufacturing; the chlorine is then returned in the form of hydrochloric acid for ethylene dichloride/vinyl chloride manufacturing

- BASF and Rubicon have guaranteed supplies of chlorine and guaranteed markets for their byproduct HCl.

Even more complex networks could, in principle be constructed. As shown in Table 14.1-1, chlorine is used in manufacturing a number of non-chlorinated products. Table 14.1-1 lists, for selected reaction pathways, the pounds of chlorinated intermediates used along the supply chain, per pound of finished product. This ranking provides one indication of the potential for networking these processes with processes for manufacturing chlorinated products (see Rudd, et al., or Chang, 1996).

Table 14.1 -1 Partial Listing of No n-Chlorinated Chemical Products That Utilize Chlorine in their Manufacturing Processes (Chang, 1996).

Product	Synthesis Pathway	Pounds of chlorinated intermediates per pound of product
Gylcerine	Hydrolysis of epichlorohydrin	4.3
Epoxy Resin	Epichlorohydrin via chlorohydrination of allyl chloride, followed by reaction of epichlorohydrin with bisphenol-A	2.3
Toluene diisocyanate	Phosgene reaction with toluenediamine	2.2
Aniline	Chlorobenzene via chlorination of benzene, followed by reaction of chlorobenzene with ammonia	2.2
Phenol	Chlorobenzene via chlorination of benzene, followed by dehydrochorination of chlorobenzene	2.1
Methylene diphenylene diisocyanate	Phosgene reaction with aniline (also produced with chlorinated intermediates)	1.5
Propylene oxide	Chlorination of propylene	1.46

An examination of individual processes, such as those listed in Table 14.1-1, can be useful in building process networks, but the individual process data do not reveal whether efficient use of chlorine is a major or a minor issue in chemical manufacturing. To determine the overall importance of these flows, it is useful to consider an overall chlorine balance for the chemical industry. The overall flows of chlorine into products and wastes, as well as the recycling of chlorine in the chemical manufacturing sector, is shown in Figure 14.1-3. The data indicate that roughly a third of the total chlorine, eventually winds up in wastes. By employing the types of networks shown in Figures 14.1-1 and 14.1-2, the total consumption of chlorine could be reduced.

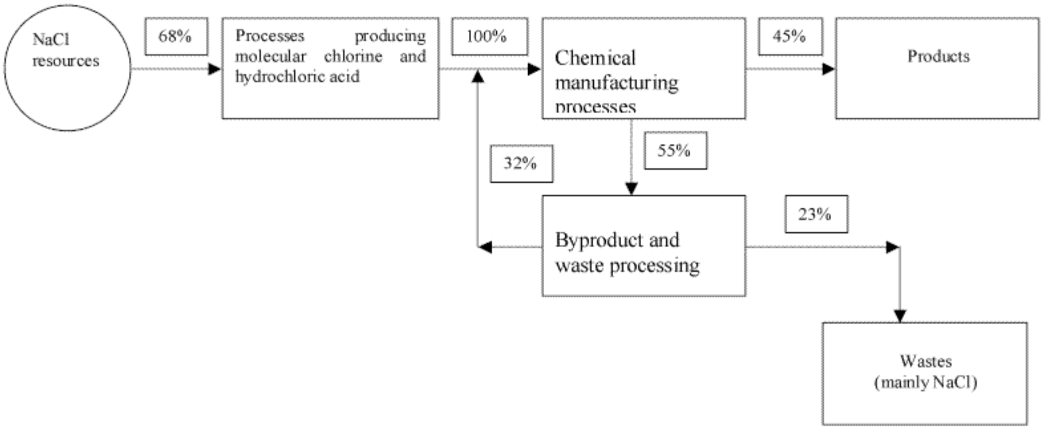


Figure 14.1 -3 A summary of flows of chlorine in the European chemical manufacturing industry (Francis, 2000).

Identifying which processes could be most efficiently integrated is not simple and the design of the ideal network depends on available markets, what suppliers and markets for materials are nearby, and other factors. What is clear, however, is that the chemical process designers must understand not only their process, but also processes that could supply materials, and processes that could use their byproducts. And, the analysis should not be limited to chemical manufacturing. Continuing with our example of waste hydrochloric acid and the manufacture of vinyl chloride, by-product hydrochloric acid could be used in steel making or by-product hydrochloric acid from semiconductor manufacturing might be used in manufacturing chemicals.

Finding productive uses for byproducts is a principle that has been used for decades in chemical manufacturing. What is relatively new, however, is the search for chemical byproduct uses in industries that extend far beyond chemical manufacturing. This chapter will examine both of these topics – the overall flows of raw materials, products and by-products in chemical manufacturing industries – as well as the potential for combining material and energy flows in chemical manufacturing with material and energy flows in other industrial sectors. Variously called by-product synergy, zero waste systems, or even industrial ecology, the goal of this design activity is to create industrial systems that are as mass efficient as possible.

Section 14.2 provides an overview of material flows in chemical manufacturing and describes analysis methods that can be used to optimize flows of materials. Section 14.3 examines case studies of exchanges of materials and energy across industrial sectors and the emerging concept of eco-industrial parks. Finally, section 14.4 briefly attempts to assess the potential benefits of by-product synergies.

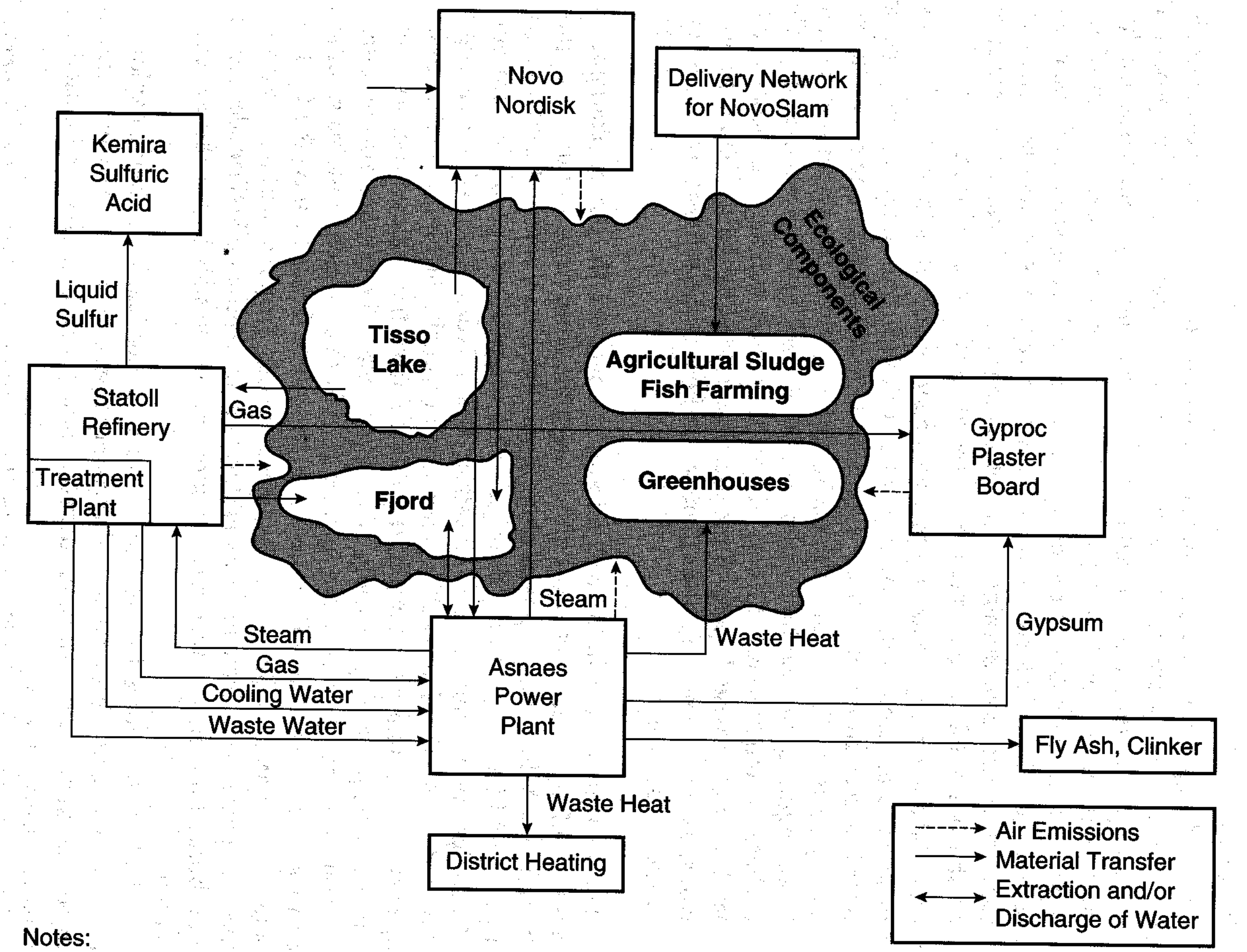
Box 1 What is Industrial Ecology?

The phrase “Industrial Ecology” evokes powerful images and strong reactions, both positive and negative. To some, the phrase conjures images of industrial systems that mimic the mass conservation properties of natural ecosystems. Powerful analogies can be drawn between the evolution of natural ecosystems and the potential evolution of industrial systems. Billions of years ago, the Earth’s life forms consumed the planet’s stocks of materials and changed the composition of the atmosphere. Our natural ecosystems evolved slowly to the intricately balanced, mass conserving networks that exist today. Can our industrial systems evolve in the same way, but much more quickly? These are interesting visions and thought provoking concepts. But, is Industrial Ecology merely a metaphor for these concepts? Is there any engineering substance to the emerging field of Industrial Ecology?

As demonstrated in this chapter, Industrial Ecology is much more than a metaphor and it is a field where engineers can make significant contributions. At the heart of Industrial Ecology is the knowledge of how to reuse or chemically modify and recycle wastes – making wastes into raw materials. Chemical engineers have practiced this art for decades. The history of the chemical manufacturing industries provides numerous examples of waste streams finding productive uses. Nonetheless, even though the chemical manufacturing industries now provide excellent case studies of Industrial Ecology in practice – networked and mass efficient processes – there is much left to be done. While the chemical manufacturing industries are internally integrated, is relatively little integration between chemical manufacturing and other industrial sectors and between chemical manufacturers and their customers.

Engineers could take on design tasks such as managing the heat integration between a power plant and an oil refinery or integrating water use between semiconductor and commodity material manufacturing. The goal is to create even more intricately networked and efficient industrial processes – an industrial ecology. Not all of the tools needed to accomplish these goals are available yet, but this Chapter begins to describe the basic concepts and suggests the types of tools that the next generation of process engineers will require.

Chapter 14 Example Figure



Notes:
(1) This figure is not drawn to scale, nor is it an accurate geographic depiction.
(2) Unused residuals resulting from all activities in the industrial ecopark are eventually released into the biosphere.

Figure 14.3-1 The industrial network at Kalundborg, Denmark. (Ehrenfeld and Gertler, 1997)

Chapter 14 Sample Homework Problem

At the Kalundborg ecopark, waste heat in the form of steam is sent from the AsnFs Power Stattion to the Statoil refinery (140,000 tons/year), to the Novo Nordisk pharmaceutical manufacturing facility (215,000 tons/year), and to district heating (225,000 tons/year). The power plant is rated at 1,500 megawatts, and the steam has a recoverable heat of 1,000 BTU/lb. Each year the power plant burns approximately 4.5 million tons of coal rated at 10,000 BTU/lb.

a) Calculate the fraction of the energy from coal combustion that goes to electricity generation, to the refinery, to the pharmaceutical plant, and to district heating. What is the total rate of energy utilization?

b) Not all of these energy demands will operate on similar cycles. Project the daily and seasonal variations in demand and suggest ways for the power plant to meet these needs.

Calculate the quantity of residential heating oil consumption that is displaced by the use of steam. If oil costs $2.00 per gallon and each gallon has a heating value of approximately 5*105 BTU, what is the value of this resource?