Annu. Rev. Energy Environ. 1998. 23:499–536

ENVIRONMENTALLY CONSCIOUS CHEMICAL PROCESS DESIGN

J. A. Cano-Ruiz and G. J. McRae
Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139; e-mail: alexcano@mit.edu, mcrae@mit.edu

KEY WORDS: pollution prevention, waste minimization, environmental indicators

ABSTRACT

The environment has emerged as an important determinant of the performance of the modern chemical industry. This paper reviews approaches for incorporating environmental issues into the design of new processes and manufacturing facilities. The organizational framework is the design process itself, which includes framing the problem and generating, analyzing, and evaluating alternatives. A historical perspective on the chemical process synthesis problem illustrates how both performance objectives and the context of the design have evolved to the point where environmental issues must be considered throughout the production chain. In particular, the review illustrates the need to view environmental issues as part of the design objectives rather than as constraints on operations. A concluding section identifies gaps in the literature and opportunities for additional research.

CONTENTS

1056-3466/98/1022-0499$08.00

INTRODUCTION

Chemical manufacturers are facing many challenges, including global competition and regulatory demands for more benign products and production processes. Environmental issues are also at the core of how the chemical industry is perceived by society. Images of dangerous pollution, reinforced by data on the generation of hazardous pollutants (1, 2), have continued to drive public perception, which in turn has put pressure on governments and regulatory agencies to tighten environmental regulations. Industry has responded to these concerns by developing programs, like Responsible Care, that establish goals for environmental health, safety, and product stewardship (3). More than 4000 companies or facilities around the world have embraced the ISO 14001 environmental management system standard. The standard requires senior management to adopt an environmental policy document that demonstrates commitment to compliance with national laws and regulations, continual improvement, and pollution prevention (4). Although the goals are certainly appropriate, the real problem and opportunity is how to translate them into action.

The enormity of the challenge can be seen in Table 1. Even just using material economy as a measure of waste generation there are wide variations across the chemical industry and obviously many opportunities for improvement. Typically, the most common way to reduce pollutant emissions has been to add control technology to bring the process into compliance with discharge standards. One consequence of this approach has been the allocation of large amounts of capital to the installation and operation of environmental control equipment (Figure 1). While there is a clear need to improve economic and environmental performance, there is unfortunately little operational guidance about how to do better. For example, consider the references listed in Table 2. These books, currently used in teaching chemical process design, contain little or nothing about environmental issues, decision making involving tradeoffs, or the larger context of the design process itself. Currently, much of the needed

Table 1 Waste generation in different segments of the chemical industry[a]

Industry segment	Product tonnage	Waste generation[b]
Oil refining	10^6–10^8	0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10^1–10^3	25–100+

[a] From References 5, 6.

[b] Results shown in kilograms of by-product per kilograms of product.

information is scattered throughout the literature. The focus of this review is to identify the issues, information sources, and approaches to process design that have the potential to lead to improvements in both economic performance and environmental quality.

THE DESIGN PROCESS

Design is a complex activity (22). It involves accepting as input an abstract description of the desires of an organization and delivering a detailed description of a concrete product, process, or system that will satisfy those desires. The

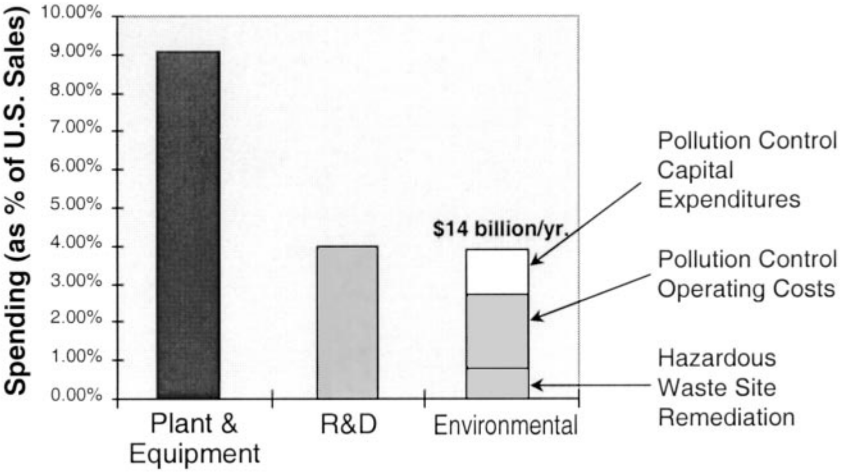

Figure 1 US chemical industry environmental expenditures in perspective (1996 data) (7).

Table 2 Approaches to environmental issues in chemical process design books

Reference	Treatment of environmental issues
Valle-Riestra (8)	States: "...the initiative to participate effectively in the struggle to preserve the integrity of the environment must ultimately originate with each engineer's inner conviction, not with externally imposed regulations..."; uses only uses economic criteria for evaluating designs
Ulrich (9)	Includes costing data for waste treatment facilities, otherwise no mention of environmental issues
Wells (10)	Advises the designer to be aware of the environmental constraints that are applicable at the project location
Douglas (11)	Stresses importance of including the cost of meeting environmental constraints in process cost estimates
Edgar & Himmelblau (12)	Optimization is restricted to economic objective functions
Baasel (13)	Includes discussion of the issues involved in determining appropriate standards; no methodologies given for evaluating the environmental merit of a design
Hartmann & Kaplick (14)	Says "[processes] must scarcely pollute the environment..."; methodologies to prevent pollution not discussed
Peters & Timmerhaus (15)	Contains section on challenges posed by environmental regulations and on "end-of-pipe" treatment technologies
Smith (16)	States "...chemical processes will in the future need to be designed as part of an industrial development which retains the capacity of ecosystems to support industrial activity and life..."; includes chapter on waste minimization and chapter on effluent treatment; includes ideas and examples for decreasing waste generation; does not include environmental evaluation methodologies
Ludwig (17)	Environmental issues not mentioned
Woods (18)	A single reference to environmental issues: "...the equipment must fit into the environment safely"
Perry et al (19)	Chapter on waste management has minimal section on pollution prevention
Biegler et al (20)	States "...environmental concerns involve satisfying the very large number of regulations the government imposes on the operation of a process."
Turton et al (21)	Includes data on waste treatment and disposal costs; adds "environmental control block" to the generic block flow process diagram; advocates pollution prevention over "end-of-pipe" treatment alternatives; includes chapter on "Health, Safety, and the Environment"; mentions pollution prevention hierarchy and life-cycle analysis; does not give specific guidance, methodologies, or examples

activity is well characterized as a decision process, involving many decision makers and multiple levels of detail. Figure 2 gives a flow diagram of the design activity. Together, the set of discrete steps shown in the figure form the design cycle. Similar diagrams have been proposed by others (e.g. 20, 23).

Design starts with problem framing. The critical importance of this step in determining the outcome of the design process is often overlooked. Design problems are rarely fully specified. Along the path from receiving a problem statement to delivering a completed design, design teams make decisions about concept definition, scope of analysis, design objectives, constraints, evaluation criteria, and stopping rules. Often framing decisions are made implicitly, by following available precedent. In a recent paper (24), Sargent recognizes the role of problem framing by distinguishing between performance models (those used in the analysis stage of the cycle) and valuation models (those used for alternative evaluation).

Once the design problem has been properly specified, the next step is the generation of alternatives. There are many different methods for generating chemical process design alternatives, including the application of existing design concepts and the generation of new ones from first principles. Because the time available to complete a design project is often limited, there is a tradeoff between the number of alternatives that are explored and the level of detail with which they can be analyzed. To reduce the severity of this tradeoff, systematic alternative generation tools, which allow a large number of alternatives to be generated and evaluated simultaneously, are utilized.

After alternatives have been generated, the next step is the analysis of alternatives. In this step, engineering analysis (usually starting with mass and energy balances) is applied to each alternative generated to make predictions about the expected performance of the system. The result of this step might be a list of the inputs and outputs of the process, including the flow rates, compositions, pressure, temperature, and physical state of all material streams, as well as the energy consumption rate from various sources. Other useful information concerns the stocks of materials in the process, as well as information related to the sizing of the equipment units.

The analysis step will produce a large number of information elements for each alternative analyzed. In the evaluation step, this information is summarized into indicators of performance that can be used to assess whether the requirements specified during the objective formulation step have been met and the extent to which the design objectives have been advanced. These indicators typically include economic indicators, such as capital investment required and operating cost, but they should also include indicators of safety and environmental performance. The evaluation step ends with a ranking of alternatives according to their overall level of attractiveness.

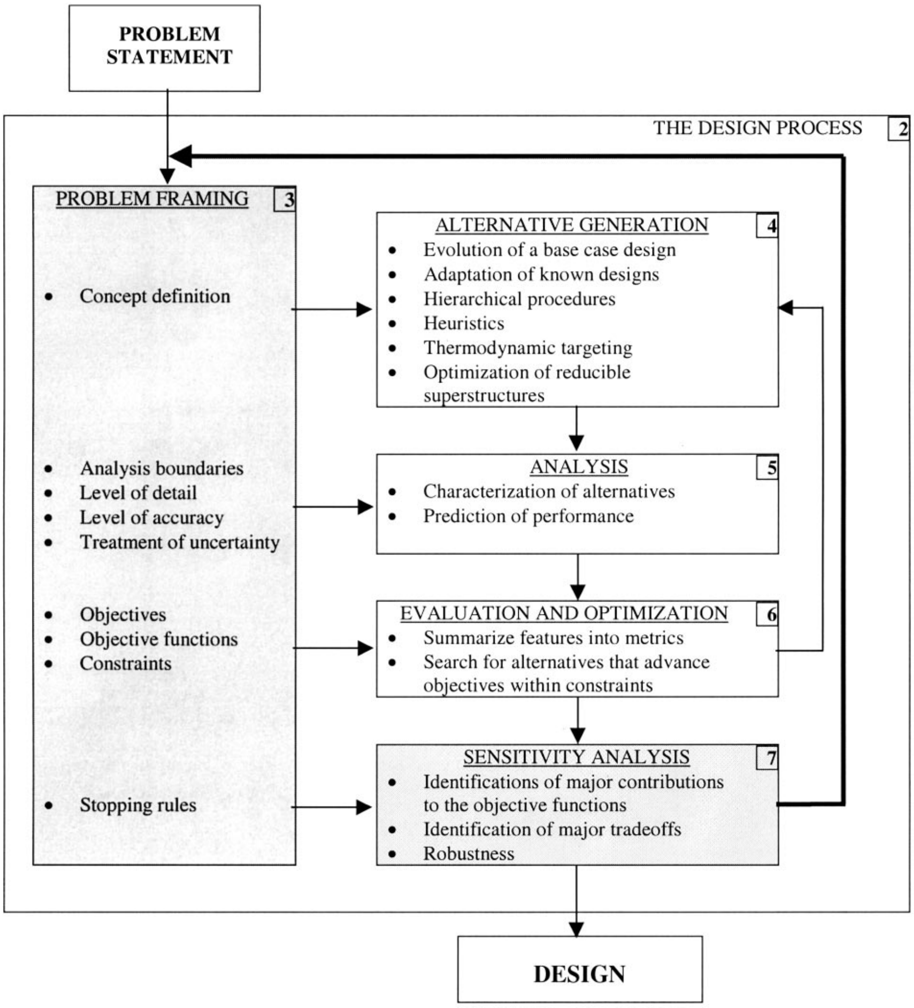

Figure 2 The design process. Given a problem statement, the design work flows according to this diagram. Each box corresponds to sections of this review in which approaches to the incorporation of environmental objectives to the steps of the design cycle are discussed. Highlighted items are often not recognized explicitly as elements of chemical process design.

Process design is iterative. Before returning to the beginning of the design cycle, the results obtained at the evaluation stage must be examined to identify opportunities for improvement. This can be done at the sensitivity analysis stage. If the design team concludes that there are no significant opportunities for improvement left available, then the work stops. Otherwise, an additional iteration on the design cycle is undertaken. Iterations might involve generating additional alternatives or modifying the framing of the problem (for example, by deciding to carry out more detailed analysis). There is a strong interaction between alternative generation, analysis, and evaluation, as depicted in Figure 2 by the inner feedback loop connecting these three activities.

The following sections of this review organize the relevant literature in terms of the steps of the design cycle. When a particular design procedure contains elements relevant to more than one step of the design cycle, we mention it only once, in the first relevant section of the review. Papers have been selected for their relevance to the design of chemical processes where avoiding environmental damage is one of the objectives of the design. Although this review focuses on process design, we must acknowledge that it is not worth investing effort in designing an environmentally benign process for the manufacture of a known environmentally hazardous chemical (e.g. the well-known cases of tetraethyl lead and chlorofluorocarbons). A recent American Chemical Society symposium–based book is a good pointer to the environmentally conscious chemical product design literature (25).

PROBLEM FRAMING

A design problem may be represented by the mathematical program:

$$\begin{aligned} &\underset{\mathbf{d},\,\mathbf{z}}{\text{Max}} \quad P(\mathbf{d},\mathbf{z},\theta) \\ &\text{s.t.} \quad \mathbf{h}(\mathbf{d},\mathbf{z},\theta) = 0, \qquad\qquad \text{(Problem DP)} \\ &\qquad\ \ \mathbf{g}(\mathbf{d},\mathbf{z},\theta) \le \mathbf{b}, \\ &\qquad\ \ \mathbf{d} \in \mathbf{D},\ \mathbf{z} \in \mathbf{Z}, \end{aligned}$$

where $\mathbf{d}, \mathbf{z}$ are the vectors of design and control variables, respectively, θ is the vector of uncertain parameters, $\mathbf{h}(\mathbf{d},\mathbf{z},\theta)$ is the vector of equations defining the process model, $P(\mathbf{d},\mathbf{z},\theta)$ is the objective function (which may be a function of multiple objectives), $\mathbf{g}(\mathbf{d},\mathbf{z},\theta)$ is the vector of equations defining the constraints on the process, $\mathbf{b}$ is the vector of parameters giving the upper bound of the constraint equations, and $\mathbf{D}$ and $\mathbf{Z}$ are the domains over which the design and control variables are defined.

Solving problem DP is only one of the activities involved in the design process. Prior to deciding on the values of the **d** variables (which given enough power and the appropriate algorithms can be done by a computer), the designer must make decisions regarding the objectives of the design (i.e. what objective functions to use and what constraints to include), the set of design alternatives to consider (i.e. the choice of decision variables to include and their domain, as well as the logical constraints relating the variables), and the scope and degree of accuracy of the model representing the problem (i.e. the functional form of the system equations). The set of all decisions made in the formulation of the optimization problem is what we call problem framing. The design process involves a series of iterations, in each of which a different version of Problem DP is solved, until such time as the designer either (*a*) is satisfied with the design or (*b*) is required to shift attention to a different design problem. Analysis at each iteration gives the designer information that can be used in the formulation of the next version of the design problem.

Figure 3 shows our view of the evolution of the framing of chemical process design problems over the past 40 years. Initially, chemical process design was limited to the design of the core reaction and separation processes. In response to the 1970s energy crisis, the domain of chemical process design was increased to include the interaction of the core process with the utility systems. Methods for heat and power integration were developed and applied to industrial problems, and today most of the chemical process design books include at least one chapter on heat integration or heat exchange network design. As the cost of complying with environmental regulations increased, chemical process designers became aware of the need to take waste generation into account in their work. Academia was slower to internalize this need and often ignored the generation of waste in the formulation of process synthesis problems. A typical example of this is a version of the second process diagram in Figure 3, published in a 1985 review of mathematical programming approaches to process synthesis (26). In that diagram, there are no outputs from the system other than the desired products.

The *bottom* panel of Figure 3 summarizes four emerging trends in the evolution of problem framing with respect to the consideration of environmental impacts.

1. Inclusion of the Waste Treatment Infrastructure in the Analysis Boundaries: It has been estimated that up to 50% of the capital for new processes is devoted to handling wastes (27). As a result, waste handling is being incorporated in the scope of process synthesis activities in industry, and efforts are being made to design processes that can use existing waste processing infrastructure, avoiding the need to invest in new treatment facilities.

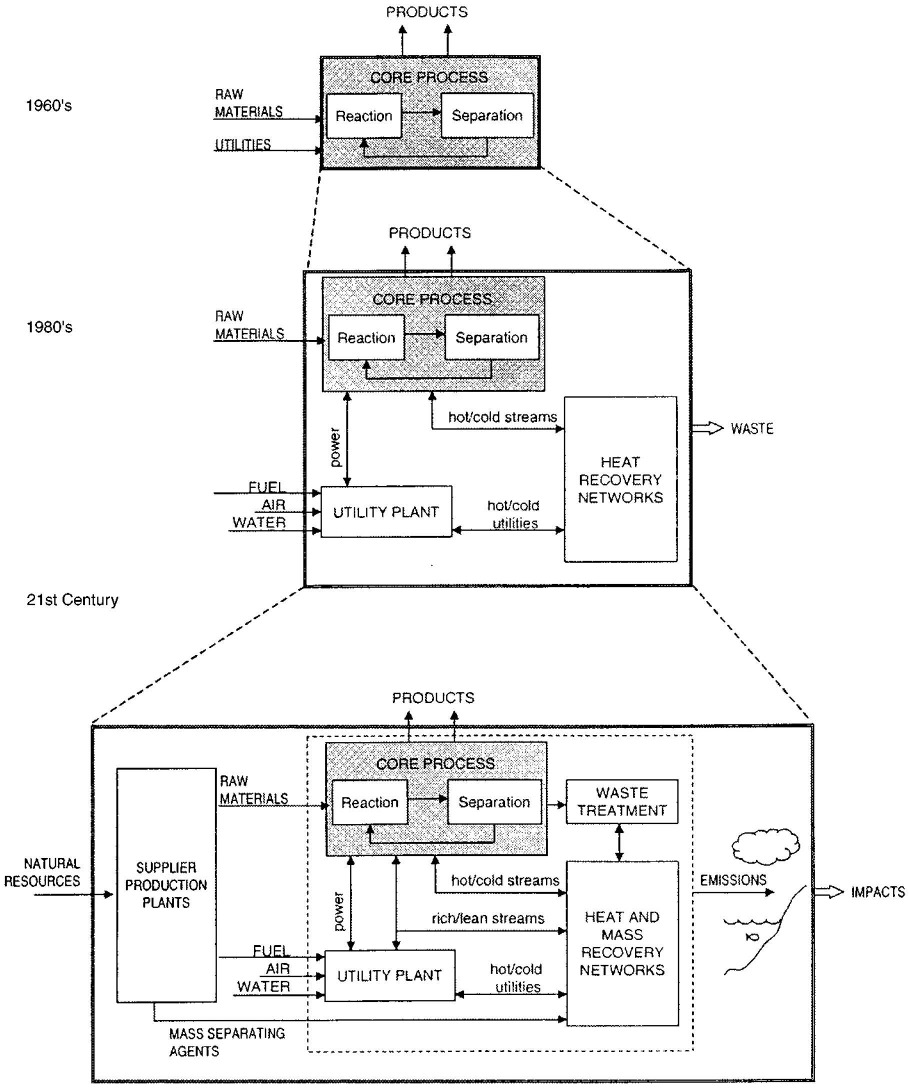

Figure 3 Evolution in the framing of the chemical process synthesis problem, from the perspective of process design. 1960's: Chemical process design only considered the core reaction and separation processes. 1980's: Incorporating heat and power integration into chemical process design revealed opportunities to decrease energy consumption at significant cost savings. 21st Century: Further incorporation of integration principles into chemical process design will reveal opportunities to decrease raw material consumption while realizing cost savings. Sustainability concerns will demand that process designers consider environmental impacts throughout the production chain.

2. Materials Integration: The success of energy integration techniques in reducing operating and capital costs (28) raised the question of whether similar savings can be achieved through materials integration. The potential savings may be overlooked if the boundaries of analysis are drawn too tightly during problem framing. It has been suggested that process design should include efforts to identify potential matches between wastes (material sources) and raw material requirements (material sinks) across processes and plants within a company (29). Materials integration techniques are being developed as a cost-effective way of reducing pollutant emissions (30).

3. Life-Cycle Analysis: Life-cycle analysis (also referred to as life-cycle assessment) is a framework for considering the environmental impacts associated with every stage in the life cycle of a product, from raw materials production to final disposal. The consequences of ignoring impacts over the entire life cycle can be illustrated by an example taken from the chemical engineering literature. In one of the first attempts to integrate environmental objectives in the design of chemical processes, Grossmann and coworkers considered the problem of synthesizing industrial chemical complexes with the two basic objectives of maximizing the net present value and minimizing the toxicity of the material flows in the system (31). The configuration they found when minimizing toxicity was one in which the production of all intermediates was carried out by suppliers. Even though the flows of toxic materials decrease within the limits of the complex under this design, the overall environmental impact could increase if the production processes of the suppliers are more polluting than those considered by the designers of the chemical complex, or if the supplier plants were located in more sensitive areas. Life-cycle thinking has been recently applied to chemical process synthesis problems in academia (32–34), and there is growing interest in its use in industry, particularly in Europe. Bretz & Fankhauser have published an account of the routine use of life-cycle assessment as part of chemical process design at Ciba Specialty Chemicals (35). A specialized computer system was developed for the purpose of integrating life-cycle inventory data for more than 4700 raw materials and 1700 products.

4. Shift in Emphasis from Effluent Concentrations to Environmental Impacts: Most environmental regulations are written in terms of effluent concentration standards. It has been noted that regulations in terms of concentrations do not give a real account of the actual emissions (36). Furthermore, design problems framed as “minimize cost subject to not exceeding allowable concentration limits” can result in using dilution of waste streams as a solution for meeting the standard without changing the amount of pollutants

released to the environment (37). Limiting effluent concentrations is only a means to achieve the end objective of improving environmental quality (38). Sharratt & Kiperstok have recently coupled environmental receptor models to the mass exchange network synthesis problem in order to pose the environmental constraint as an environmental quality standard, instead of as an effluent concentration standard (39,40). The idea has also been applied in industry: Amoco used exposure to benzene in the vicinity of its Yorktown refinery (determined through environmental modeling) as a criterion for ranking pollution prevention projects (41).

GENERATION OF ALTERNATIVES

The design of chemical processes with lower environmental impact starts with an understanding of the sources of emissions and waste in chemical processes. Figure 4 [adapted from Lerou & Ng (42)] is an abstraction of a chemical process in which raw materials are processed into desired products. By-products may be generated either as a result of the desired reaction stoichiometry or as the consequence of undesired secondary reactions (selectivity losses). Unwanted by-products may also be generated in the separation system (e.g. by polymerization reactions in distillation column reboilers). Purge streams are necessary to prevent the accumulation of trace components in recycle streams, unless these components can exit the process in the product or by-product streams. Other materials introduced to the process include reaction agents (e.g. catalysts, solvents, diluents, heat carriers) and separation agents (e.g. solvents, adsorbents, entrainers), which contribute to waste generation because they degrade with time and may exit the process with the purge or by-product streams. Leaks (known in the literature as "fugitive emissions") may occur anywhere in the system. In addition, emissions are produced in the systems that provide utilities to the process.

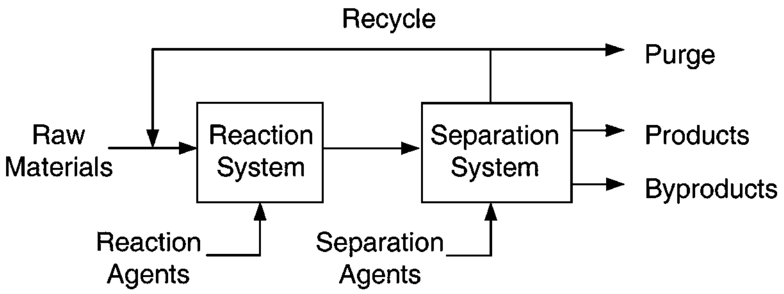

Figure 4 Material flows in a chemical process.

The term zero-avoidable pollution (ZAP) has been coined to refer to the by-product waste generated in processes in which all raw materials, reaction agents, and separation agents are recycled with 100% efficiency (43). It is worth noting that ZAP designs are not necessarily designs with minimal environmental impact. There are two reasons for this: First, separation and recycling require energy, and there are emissions associated with the supply of energy to a process (e.g. emissions from fuel combustion); and second, the quantity and composition of by-product waste generated in a ZAP design can be changed by changing the reaction path or by changing the design of the reactor network. Examples of alternative "green" synthesis pathways to a large number of chemicals have been reported (44, 45).

The goal of environmentally conscious alternative generation is to produce designs that (*a*) have high economic potential, (*b*) have high conversion of raw materials into desired products, (*c*) use energy efficiently, and (*d*) avoid the release of hazardous substances to the environment. The key to the discovery of such designs is process integration (energy integration, materials integration, and processing task integration). Pollution from a chemical process can be viewed as the consequence of using the environment as a sink for unwanted by-products and unrecovered materials. Using nonrenewable resources as a source of raw materials for a process raises issues of sustainability. It follows from these observations that design alternatives that increase the use of process units and streams as material sources and sinks may have lower environmental impact. There are well established energy integration techniques that reduce utilities consumption by using process streams as sources and sinks of heat (28). The use of processing task integration in reactive distillation processes has been shown to reduce costs, energy use, and emissions (46, 47).

Framing of the problem influences the range of alternatives that may be considered, through the decisions made during concept definition. A narrow concept definition may fix prematurely the process chemistry or it may limit the type of unit operations considered (e.g. it may restrict the design team to using conventional, well-proven technologies).

Reviews of methodologies to generate design alternatives with pollution prevention as an objective have been given by Manousiouthakis & Allen (48), Rossiter & Kumana (49), and Spriggs (22, 50). The classification of approaches that follows is partly based on the discussion presented in these references.

Use of Documented Pollution Prevention Solutions as a Source of Design Alternatives

Ideas for reducing waste generation in chemical processes have been published in professional journals (51–58). These ideas range from general questions intended to elicit ideas to very specific process and equipment changes. Two particularly comprehensive collections of ideas have been assembled by Nelson

(59) and Smith et al (60–65). Englehardt compiled a list of references to pollution prevention technologies and classified them according to their placement in the pollution prevention hierarchy and the function of the industrial hazardous materials involved (66). Government agencies compile and publish ideas for preventing pollution in specific industry sectors from time to time (e.g. 67–70). Electronic databases have been created to enable designers to search for solutions that are most relevant to their applications (71,72).

Design by Case Study

In designing by case study, process models are used to simulate the performance of an existing process or a base case design. The design team next thinks of process modifications that may improve system performance. The process model is modified to incorporate the proposed changes, and simulations are carried out to check whether the desired performance improvements are realized in the model. With the availability of process simulators (e.g. Aspen Plus), this approach to process design has become widespread. Examples of applications to pollution prevention have been published (73–83). Process modifications explored by this technique are usually incremental in nature.

Hierarchical Design Approaches and Other Methods of Structured Thinking

Douglas (84) applied his hierarchical process synthesis procedure to the problem of identifying potential pollution problems and identifying process alternatives that can be used to eliminate these problems. The recommendations obtained by his procedure are fairly general (e.g. change the chemistry, change the solvent, look for a different separation system) and serve as a starting point for the search of design alternatives. The procedure has been used to classify process improvements reported in the literature according to the sources of waste and the waste minimization techniques applied (85). Rossiter and coworkers built on the procedure by adding more key questions at each decision level and used it to generate attractive alternatives for reducing waste generation and emissions from the fluid catalytic cracking unit at Amoco's Yorktown, VA, refinery (86). More recently, Douglas expanded his set of synthesis rules for the design of separation system flow sheets for vapor/organic liquid/aqueous liquid/solid mixtures (87). The rules acknowledge explicitly the generation of waste streams and provide some guidance for addressing the pollution problems arising from these streams.

Pinch Analysis and Other Targeting Techniques

Pinch technology was first developed as a tool for reducing the capital and energy costs of a processing plant through the design of heat exchanger networks. It is most often used to design the heat recovery network of a process, once the core reaction and separation processes have been defined. Pinch technology recognizes that in the majority of chemical processes there exist heat sources (hot process streams that need to be cooled) and sinks (cold streams that need to be heated). Instead of using utilities (e.g. steam, cooling water) to bring all process streams to their desired temperatures, pinch technology exploits the heat sources and sinks in the process before using utilities, thus reducing the operating cost of a design. A key feature of the pinch design method is that minimum utility consumption targets and approximate capital costs of the associated heat exchanger network can be established prior to the development of a design. Another key feature is its use of diagrams to identify integration opportunities within a process, a plant, or a total site. A review of the state of the art in pinch analysis up to 1994 is given by Linnhoff (28). Buehner & Rossiter have reviewed the application of pinch analysis to waste minimization problems (88). Reducing energy consumption in a plant can be translated into reduced flue gas emissions (for a given fuel and combustion technology type), since less fuel needs to be burned (89). BASF (Badische Anilin Soda & Fabrik AG) reported the results of an energy efficiency campaign undertaken at their Ludwigshafen plant in the early 1980s (90). Their efforts resulted in significant reductions in the generation of CO_2, SO_2, NO_x, CO, ash, and wastewater, despite increased production levels.

Minimizing energy consumption may not always result in minimizing the environmental impact of utility systems. Smith & Delaby argue that the established methods for targeting the minimum energy consumption of a given process do not necessarily give insights into the emissions of combustion products associated with supplying the heat and power needed by the process (36). They argue that considering global emissions (emissions generated by fuel combustion on-site at furnaces, boilers, and gas turbines and off-site at power generation plants) gives a broader view of the pollution problem and is the view that should be universally adopted.

Many separation processes are driven by heat inputs (e.g. distillation, evaporation) or by heat removal (condensation, crystallization). When such processes are used to recover materials from waste streams, thermal pinch analysis can be used to minimize the cost and emissions associated with the separation. Smith et al have given examples where energy savings are achieved by integrating materials recovery and waste treatment units with the rest of the process (89). Richburg & El-Halwagi developed a shortcut method for the cost-optimal design of condensation networks for the recovery of volatile organic compounds from air, based on pinch analysis concepts (91).

El-Halwagi exploited the analogy between mass and heat transfer to develop the concept of mass exchange network synthesis, based on the pinch method for heat exchanger network synthesis (92). He developed tools analogous to those used in thermal pinch analysis (composition interval diagram, composite curves, grid diagram) and applied to a sample problem. A mass exchanger can be any direct-contact countercurrent mass transfer operation, such as absorption, adsorption, liquid-liquid extraction, ion exchange, leaching, and stripping (30). As applied to pollution prevention, the goal of mass exchange networks is to transfer species that are potential pollutants in effluent streams to streams in which they may have positive value (47). The idea of matching material sources and sinks has been further elaborated by El-Halwagi and coworkers in the concept of waste-interception networks (93). The main goal of these networks is to provide selective interception and rerouting of undesirable species that would otherwise exit a process to those parts of the process that can act as sinks for these species.

Wang & Smith developed a pinch design methodology for wastewater minimization using the more general mass exchange network framework as a basis (94, 95). Processes that use water are represented as limiting water profiles in a concentration versus mass load diagram, which is analogous to the temperature versus enthalpy diagram used in the design of heat exchanger networks. The limiting water profile for a process represents the minimum amount of water with the highest possible concentration of contaminants that would be able to perform the task required in that process and is not necessarily the actual water profile that will be used in the final design. Pinch analysis techniques are then used to establish targets for minimum freshwater use (enabling reuse of water in processes that tolerate higher contaminant concentrations) and to design networks consistent with those targets. The methodology includes the possibility of water regeneration (treatment) and recycling and can be used in problems that involve multiple contaminants. An extension has been developed that makes the methodology applicable to batch processes (96). The same framework was used to develop a methodology for the design of distributed effluent treatment systems, which seek to minimize the cost of achieving specified concentrations in the wastewater effluent of a site by segregating wastewater streams, combining them when economies of scale are attainable, and matching streams to treatment processes (97). Dhole et al have developed a similar methodology, trademarked WaterPinch (98). In this method, water sources and demands are plotted in a purity versus water mass flow rate diagram. Composite curves are developed for the sources and the demands, and the pinch point is located. Freshwater and wastewater targets can be read directly from the diagram, once the composite curves have been brought together at the pinch point. Pinch analysis techniques have been applied to industrial wastewater minimization problems (99–101).

Other targeting approaches have been developed for the minimization of waste generation in the core reaction and separation processes. Flower and coworkers have developed tools for establishing mass-efficiency targets for reaction and separation systems (102, 103). By using the concept of the attainable region for reactors and the assumption of sharp splits for separators, they develop lower bounds on the mass of waste by-products that can be obtained for a given reaction scheme. Ahmad & Barton presented a methodology for the automatic targeting of maximum feasible solvent recovery from streams with an arbitrary number of components by batch distillation (104).

Mathematical Programming

In the mathematical programming approach to process synthesis, a reducible superstructure is optimized to find the best combination of process units that achieve the design task. Manousiouthakis & Allen reviewed several process synthesis concepts and outlined their importance for waste minimization (48). Their task definitions and examples of the application of mathematical programming to waste minimization under each task are summarized in Table 3.

There is a large number of published mathematical programming formulations of the problem of synthesizing recycle/reuse networks for waste reduction. Although direct contact mass exchangers are used in the majority of these formulations (37, 92, 113, 119–125, 129–131), other unit operations have also been used, including condensers (112, 115–117) and pressure-driven membrane units (113, 114, 132). The scope of applications include the following: single (37, 112, 113, 115, 117, 119–123, 131, 132) or multiple (116, 125) transferrable pollutants; linear (37, 113, 119, 120, 123, 125, 131), convex (121), or general nonlinear (122) equilibrium functions; fixed (112, 115–117, 119–123, 125, 132) or variable (within bounds) (37, 114, 124, 131) recovery targets; physical (37, 112–117, 119, 120, 124, 125, 129, 131, 132) or chemically reactive (121, 122) separations; inclusion of mass separating agent regeneration unit operations in the network (120); and inclusion of flexibility constraints (131).

A common feature in these formulations is the use of cost minimization as the objective function in the optimization. Earlier formulations used a two-stage optimization procedure (37, 112, 119–123, 125). First, operating cost minimization is used to establish minimum utility consumption targets. This is followed by the solution of a mixed integer linear programming transshipment problem to design a network with the minimum number of units that meets the minimum operating cost targets. More recent formulations use a total cost minimization approach, where capital costs are included in the objective function (114–116, 123, 124, 132). Both types of objective functions include only the cost side of the profit equation. As the value of recovered materials is not included, opportunities to improve the economic performance of these networks by increasing material recovery beyond targets specified in the framing of the optimization problem may be overlooked.

Table 3 Process synthesis tasks and references to examples of their application to waste minimization problems using the mathematical programming approach

Task	Task definition (48)	References
Material synthesis	Given set of desirable properties, identify material that possesses these properties	105–108
Reaction path synthesis	Identify reaction path that employs substances from set of permissible chemicals to yield desired product (meeting economic, thermodynamic, and kinetic constraints)	107, 109, 110
Reactor network synthesis	Given reaction mechanism, identify network of reactors in which reactions transform raw materials to products at optimum venture cost	111
Separator network synthesis	Given a set of multicomponent feed streams, identify network of separators that can yield set of desired product streams at minimum venture cost	112–117
Recycle/reuse network synthesis	Given set of multicomponent waste streams, identify network of separators that allow the recycle of waste streams (meeting quality specifications) at minimum venture cost	93
Heat exchanger network synthesis	Given set of hot and set of cold streams, identify network of heat exchanger units that can transfer heat from hot to cold streams at minimum venture cost	118
Mass exchanger network synthesis	Given set of rich streams and set of lean streams, synthesize network of mass exchange units that can transfer certain species from rich streams to lean streams at minimum venture cost	37, 92, 113, 119–126
Total flowsheet synthesis	Given reaction path that transforms new materials to desired products, identify network of process units that accomplishes transformation at minimum venture cost	32, 75, 127, 128

Expert Systems and Other Artificial Intelligence Approaches

Huang & Edgar listed features of the problem of generating waste minimization alternatives that make knowledge-based expert systems and fuzzy logic attractive tools for designers (126, 133). (*a*) Incorporating environmental objectives into process design requires knowledge from many disciplines. Thus, the task is knowledge intensive. (*b*) The generation of waste minimization options is heavily dependent on experience, and quantitative descriptions of the processes generating waste are often not available. Hence, qualitative information needs to be incorporated in the analysis. (*c*) The available information pertaining to the environmental impact of a process is often uncertain, imprecise, incomplete, and qualitative in the design stage. (*d*) A large number of regulations and strategies for pollution prevention may be expressed as rules.

One of the major barriers to process integration is the perception that highly integrated processes are difficult to control. Huang & Fan addressed this problem by developing a hybrid intelligent design system that improves the controllability of heat and mass exchanger networks by choosing stream matches that improve an index of controllability while keeping the operating cost of the network at its minimum (130). Their system combines pinch analysis for the generation of targets with an expert system, fuzzy logic, and neural networks to assign stream matches.

Computer-assisted systems for the rapid generation of alternative synthesis paths to a desired chemical are available (e.g. SYNGEN, LHASA). Their use in supporting pollution prevention initiatives has been explored by government agencies (134) and as teaching aides (135).

The EnviroCAD system has been developed at the New Jersey Institute of Technology as an extension of BioDesigner, a program for the design and evaluation of integrated biochemical processes (136). The system takes as input data a set of waste streams and recommends alternatives for waste recovery, recycling, treatment, and disposal based on three knowledge bases. An expert system for generating feasible treatment trains for waste streams has also been embedded in the Process_Assessor module of the BatchDesign_Kit under development at the Massachusetts Institute of Technology (43, 137, 138). The expert system is based on heuristic rules containing knowledge of regulations and treatment technologies.

ANALYSIS

The function of the analysis step is to generate the information needed to evaluate the merit of a design. A challenge for designers interested in incorporating environmental considerations into their work is that much of the information needed to evaluate the environmental impact of a proposed design alternative is not normally generated in the analysis stage, when economic performance is the only design objective. Consider the case of fugitive emissions. Fugitive emissions are losses of process fluids through leaks in equipment. Although these losses are strongly influenced by the choice of equipment and operating procedures, decisions made at the conceptual design stage (e.g. temperature, pressure, and flow rate of recycle streams) are also important contributing factors. Fugitive emissions are usually too small to impact the process mass and energy balances (typically 500–1500 g/Mg of product) (47), but in some plants it has been estimated that fugitive emissions are responsible for 70–90% of the environmental releases of hazardous substances (139). Because the value of the materials lost through fugitive emissions can be neglected in the economic evaluation of a process, no effort is made during process design to estimate the magnitude of fugitive emission losses. However, such estimates may be important in determining the environmental merit of competing design alternatives. Another example is that of selectivity losses in reactors. From an economic perspective, all that is needed during the analysis stage is an estimate of the amount of raw materials converted to unwanted by-products, and an estimate of the resources needed to separate the unwanted by-products from the desired product. Estimation of the amounts of individual by-products is usually not required. However, two processes with the same selectivity to the desired product may have different environmental impacts, depending on the composition of the unwanted by-product stream. Thus, the set of chemical species considered in the analysis may have to be expanded beyond the set used when economic performance is the only evaluation criterion.

Not all mass and energy balances that are relevant for estimating the pollutant emissions from a process are included in the standard flow sheets used during process design. For example, although energy consumption is typically quantified, the emissions associated with the generation of electricity or steam of various grades typically are not. In addition, environmental concentrations of released pollutants may be necessary for a proper evaluation of the potential environmental impact of a design. In this case, the material balances used to evaluate the process need to be expanded to include the fate and transport of environmentally sensitive species.

It has been noted (136, 140) that commercial process simulators are still deficient in predicting chemical species concentrations in dilute process effluent or waste streams. Unit operation models for innovative separation technologies (e.g. membrane separations) and waste treatment equipment are not included in commercial process simulators and are therefore usually not included in conceptual process designs. Farag and colleagues described the structure of models of pollution control and waste treatment processes they developed using the Aspen Plus simulator (141). They noted that a challenge in the development of these models is that they often involve the handling of types of materials that are not well characterized.

EVALUATION OF ALTERNATIVES

The central question in process evaluation within an environmentally conscious design framework is how to evaluate design alternatives from an environmental perspective. A related question is how to balance environmental objectives with other design objectives.

Problem framing has a direct impact on this step of the design cycle. When the problem is framed, decisions are made with respect to objectives that the design should advance and, in particular, about the objective functions that will be used to translate the data produced during the analysis step into aggregate metrics than can be used to optimize and rank design alternatives.

A quantitative evaluation of a process flow sheet involves summarizing the information generated during the analysis stage of design into a few metrics that can be used to optimize and rank design alternatives. An example of a metric used for economic evaluation is the net present value (15). This allows a design team to summarize into a single number information regarding production and consumption of materials and utilities, as well as to design specifications for equipment. The additional information needed are unit prices for materials and utilities, correlations that relate equipment design specifications to their installed cost, and the discount rate used by the firm to make trade-offs between capital spent in the present and future cash flows.

In contrast to the calculation of net present value, where all the additional information needed to summarize flow-sheet information into a single metric can be obtained from company databases, market data, or vendors, no such information is available to chemical process designers to allow the computation of an overall widely accepted index of environmental performance. There are three main reasons for this. (*a*) Relevant properties of chemicals (e.g. toxicity, environmental degradation constants) are not readily available in the tools commonly used by chemical engineers (process simulators, chemical process design handbooks). The properties have not been measured for a large number a chemicals, and the measurements that have been made frequently show wide ranges of variation. Although structure-activity relationship tools exist for estimating the toxicity of chemicals for which biological assays are not available (142), the accuracy of their predictions needs much improvement. (*b*) With the exception of environmental problems that are global in nature (e.g. ozone layer depletion and greenhouse gas concentration increases), location-specific knowledge is needed to estimate potential environmental impacts. This is particularly challenging when trying to estimate the environmental impact of the production of inputs obtained from external suppliers. (*c*) People differ in the importance they assign to various environmental impacts. This is a matter not of disagreement about facts but of differences in values.

Environmental Concerns as Constraints on Economic Optimization

The most common approach to incorporating environmental considerations in chemical process design has been to treat them as constraints: Upper limits are set for pollutant flows or concentrations in waste streams (based on regulatory requirements), and designs that satisfy these constraints are evaluated in terms of economic indicators, such as net present value (75), annualized profit (128, 143), payback period (50), operating margin (74, 110), total annualized cost (91, 95, 97, 112–116, 119, 124, 129, 131, 132, 144–146), or operating cost (37, 48, 91–93, 116, 120–122, 125, 133). The search for economically attractive waste minimization design alternatives is advanced by including the cost of waste treatment and disposal in the economic objective function (74–76, 84). The costs associated with the retirement of process equipment and site restoration at the end of the useful life of a process have usually not been included in the analysis.

Surprisingly, the value of products, by-products, and recovered materials is often not included in the objective function, as the majority of authors have chosen to use cost minimization as their economic objective. Depending on how the optimization problem is framed, this may lead to overlooking opportunities to increase the profitability of a design by recovering materials from waste streams beyond the level required by compliance.

The main problem with incorporating environmental considerations as constraints on the flow or concentration of chemical species in particular waste streams is that the proposed solutions may not address the underlying environmental concern. This is illustrated by the examples given in a couple of papers addressing the synthesis of membrane separation networks for waste reduction (113, 132). The proposed networks split an aqueous waste stream into two streams, one of which has a pollutant concentration low enough to meet the specified discharge limits. However, neither the fate nor the treatment cost of the concentrated stream is considered in the solution.

A variation of this approach is to optimize for economic performance while setting environmental objectives in terms of environmental quality standards in a particular receptor (e.g. a water body or the airshed in an urban area) (39, 40). Although this approach presents opportunities to achieve the desired level of environmental protection at lower social cost, it poses challenges to individual firms because their allowable emissions or discharges would be affected by those of other firms sharing the same receptor.

Environmental Concerns as Objectives

Instead of treating environmental considerations as constraints, designers can choose to treat them as an objective to be balanced against other objectives in the design (31–33, 43, 81, 111, 118, 128, 143, 147). This requires establishing environmental performance measures. Several authors (148–150) have noted that the lack of metrics to support objective environmental assessments is one of the main barriers to developing effective pollution prevention and design for the environment approaches. Linninger and coworkers pointed out that the lack of a general binding value system for environmental impact assessment makes it difficult to evaluate the environmental impact of a design (138). Given the diversity of prevailing views regarding the environment, such a binding value system may never become available.

MINIMIZATION OF EMISSIONS OF POLLUTANTS OF CONCERN In cases where the emission of a single pollutant is the most important environmental concern affecting a design, the mass of pollutant released into the environment can be used as an indicator of environmental impact. Such an approach has been used to study the trade-off between control cost and emissions of nitrogen oxides from a power plant (151) and a refinery (145). Some authors have chosen to use carbon dioxide emissions as a measure of flue gas emissions from power generation (36) or associated with utilities used in chemical production (76).

When more than one chemical is a source of environmental concern, environmental evaluation becomes more complicated. One approach is to use the release inventory directly as a set of indicators. This may be an acceptable solution when only a few pollutants are involved. As an example, Chang & Hwang use emissions of CO_2, SO_x, and NO_x as three independent environmental objectives to be minimized in the design of utility systems for chemical plants (118). The approach becomes unmanageable when upstream emissions are considered, as is done in life-cycle analysis. It is not uncommon for life-cycle inventories to contain releases and discharges of dozens of different species. In such cases it is clearly necessary to summarize the information into a small number of indicators that can be used to optimize and rank alternatives.

MINIMIZATION OF MASS OF WASTE GENERATED It has been argued that mass is the only consistent and universal basis for aggregating waste streams (78). Indeed, indicators based on the mass of waste generated are the ones most commonly used in the chemical engineering literature. Examples of indicators used are the total mass of waste generated (104, 111, 128, 143, 152), the mass of waste generated per unit mass of product (5, 6, 77, 78, 81–83, 153–155), and the mass of waste generated as a percentage of the total mass of outputs from a process (156).

If waste minimization is understood as reducing the mass of waste generated in the production of a product, the mass-based indices used in the references cited above are suitable indicators for the objective of minimizing waste. However, waste minimization is a means, not an end. The goal is improved environmental quality (157). In seeking to avoid value judgements regarding the relative environmental impact of different chemicals, some authors go to the extreme of including inert substances such as nitrogen in flue gases in the computation of the mass of waste generated (152). Clearly, chemical process designers should take into account the difference between the emission of 1 kg of N_2 and the emission of the same amount of a highly toxic chemical.

Recognizing that not all substances in a waste stream raise the same level of concern with respect to their environmental impact, some authors compute total mass of waste in special categories of concern (43, 154, 158, 159). Common categories include regulated hazardous waste, volatile organic compounds, and substances included in regulatory lists, such as the *Toxic Release Inventory in the United States*. In the system used at Polaroid Corporation, all materials used or generated by the company are placed in one of five categories, according to their potential hazard (160). The total mass of materials used (in the case of the two most sensitive categories) or contained in waste streams (in the case of the other three categories) is reported separately for each category.

Although the approach mentioned above is a step in the right direction, it still falls short of what is needed to incorporate environmental considerations into the evaluation of a design. The reason is that the contribution of a unit of mass emission to a particular environmental impact may vary by orders of magnitude among the chemicals included, even in narrowly defined categories. The alternative is to shift the focus from emissions to impacts.

MINIMIZATION OF CONTRIBUTION TO SPECIFIC ENVIRONMENTAL PROBLEMS In the problem-oriented approach, the relative contributions of different chemical species to identified environmental problems are used to obtain a weighted sum of the masses of chemicals emitted. The resulting figure can be interpreted as the mass emissions of a single reference substance that would have the same contribution to an environmental problem of concern as the particular mix of emissions being analyzed. For example, emissions of different greenhouse gases may be aggregated into an index by multiplying the emissions of each gas by its global warming potential relative to CO_2 (161).

The first attempts to apply the problem-oriented approach in the development of environmental indicators for the evaluation of chemical processes focused on toxicity. Grossmann and coworkers multiplied the material flows in a chemical process by the inverse of the 50% lethal dose of each material and added the resulting figures to obtain a toxicity index (31). In a study of the structure of the petrochemical industry that would minimize the toxicity of organic pollutant emissions, Fathi-Afshar & Yang (147) divided material flows by their threshold limit values (TLVs) [upper limits to the concentration of pollutants in air in the work environment recommended by the American Conference of Governmental

Industrial Hygienists (162)] and multiplied them by their vapor pressure (they assumed that fugitive emissions are proportional to vapor pressure). TLVs were also used by Horvath and coworkers as the basis for a toxic emissions index (163).

Literally dozens of different ranking and scoring schemes have been proposed to evaluate chemicals based on measures of toxicity or measures of toxicity and exposure (164). These systems differ in the scoring criteria used, the endpoints used to score each criterion, the algorithm used to aggregate individual scores into an overall score, and the procedures used to score chemicals with missing data. The hierarchy of indicators proposed by Jia and coworkers (171) (see Table 4) gives an example of the different levels of sophistication that can be used to evaluate the potential toxic impacts of a design. The fourth type of index is based on the PEC/PNEC (Predicted Environmental Concentration/ Predicted No Effect Concentration) concept used for risk characterization (165)

Table 4 Toxicity-based indicators for the evaluation of environmental release[a]

Aspects considered	Example
Mass	$Q_{1m}\sum_{c} E_{c,m}$ $Q_{i,m}$ is a toxicity-based environmental indicator for chemical releases to medium m; $E_{c,m}$ is the mass of chemical c released to medium m
Mass + toxicity	$Q_{2m} = \sum_{c} \frac{E_{c,m}}{C_{c,m}}$ $C_{c,m}$ is the toxicity-based reference concentration of chemical c in medium m; examples include the threshold limit value, 50% lethal concentration, and predicted no-effect concentration; other measures of toxicity can be used instead of reference concentrations (e.g. reference doses and cancer potency factors)
Mass + toxicity + persistence	$Q_{3m} = \sum_{c} \frac{E_{c,m}\tau_{c,m}}{C_{c,m}}$ $\tau_{i,m}$ is the persistence of chemical c in medium m and depends on the rate of the chemical loss by advection, reaction, and transfer to other media
Mass + toxicity + persistence + environmental mobility	$Q_{4m} = \sum_{c} \frac{\left(\sum_j E_{c,j}F_{c,j,m}\right)\tau_{c,m}}{C_{c,m}}$ $F_{c,j,m}$ is the intermedia mobility fraction of chemical c from medium j to medium m; the values of $\tau_{c,m}$ and $F_{c,j,m}$ are context specific; estimating these values requires either the use of a multimedia mass balance model or a broad database of chemical fate observations

[a]Adapted from Jia et al (171).

and has been characterized as the most consistent with an environmental science approach (166). Cave & Edwards recently applied an index of this type to compare the environmental hazard of six alternative routes with the production of methyl methacrylate, based on the total inventory of chemicals present in the corresponding plants (167). Variations of these indices that take into account bioaccumulation in the food chain have been developed (168, 169). A further level of sophistication is embedded in the Human Toxicity Potential index developed by Hertwich and coworkers (170). In addition to toxicity, persistence, and environmental mobility, this index takes into account the relationship between environmental concentrations and chemical doses received through different exposure routes.

Toxicity is not the only environmental concern relevant to chemical process design. Other relevant environmental problems to which a chemical process may contribute include ozone layer depletion, climate modification, acid precipitation, and photochemical smog formation. Stefanis and coworkers (32, 33, 107) and Kniel and collaborators (34) applied such problem-oriented indices to the design of chemical processes.

MINIMIZATION OF OVERALL INDICATOR OF ENVIRONMENTAL IMPACT Efforts have been made to develop an overall index of environmental impact for use in the quantitative evaluation of chemical process flow sheets (79, 80, 172). Chemical process designers willing to use such indices must keep in mind that these indices are meaningless without input from the users about their values regarding the environment. The Eco-indicator 95 is an example of an environmental indicator developed for product design applications where the method developers have been explicit about the value judgements used to weight contributions to different environmental damages (173). The method developers are also explicit about the decisions they made to include or exclude environmental-problem categories in their indicator (for example, they excluded local toxic impacts because their focus was on environmental effects on a European scale). The weighting factors used in the Eco-indicator 95 are developed in two stages. First, individual problem-oriented indicators are normalized by the indicators corresponding to the emissions inventory of Europe. In the second stage, normalized scores are multiplied by reduction factors. The reduction factor for a particular problem is defined as the factor by which the current European emissions would have to be reduced so that the resulting impact would not exceed 1 death per million people per year, or a 5% ecosystem impairment. The method developers are explicit in expressing their value judgement that 1 death per million people per year is equivalent to a 5% ecosystem impairment. Users who do not share that value judgement would need to develop their own reduction factors for each problem.

Table 5 Environmental indicators used for process evaluation in the chemical industry

Company	Environmental index used	Comments
Roche (153)	Total mass of waste (before end-of-pipe treatment) per unit mass of end product	
3M (156)	Total mass of waste as fraction of the total mass of outputs of a process (including products, by-products and wastes)	
Polaroid (160)	Total mass of chemical use or waste in each of five categories per standard unit or product	All chemicals in raw materials and waste are assigned to one of the five categories, based on relative hazard
Rohm and Hass (175)	Weighted sum of waste stream masses, per unit mass of product	Weighting factors are the product of toxicity score (based on its NFPA health hazard rating) and a "mode of delivery to the environment" score (based on whether the waste stream is directly discharged, treated before release, or recycled or reused)
Imperial chemical industries (176)	Equivalent emissions of reference substance for ten environmental impact categories	Potency factors for each category are developed based on published studies and standards
Ciba Specialty Chemicals (35)	Eco-indicator 95 (173) and Swiss Eco-scarcity method (177)	The toxicity of most chemicals is not considered in either indicator; Eco-scarcity method based on national emission targets established by the Swiss government

INDUSTRIAL PERSPECTIVE A sample of environmental indicators being used to evaluate processes in the chemical industry are given in Table 5. DeSimone & Popoff have published a book with accounts of the approaches used by a wide variety of firms to measure their environmental performance (174).

Trading Off Environmental Objectives Against Other Design Objectives

The selection and refinement of a final design is a multiobjective decision problem, where economic, environmental, and safety concerns may be in conflict (42). As explained above, "the environmental objective" is in itself a collection of many objectives, where improving one objective may not be possible without worsening another. For example, decreasing solvent emissions by increased separations and recycling may lead to increased emissions of combustion gases from energy generation.

The first step in the analysis of a decision problem with multiple objectives is the identification of the set of nondominated alternatives, also known as the Pareto set of noninferior alternatives (43). A dominated alternative is one that is inferior to another feasible alternative in the set with respect to all attributes under consideration. This means that for each dominated alternative there is at least one win-win alternative that can be attained without sacrificing achievement in any of the design objectives. The set of alternatives that remains after all the dominated alternatives have been removed is the set of nondominated alternatives. Techniques for identifying the set of nondominated alternatives include the ε-constraint technique and the weighting method approach. Both of these techniques have been applied to process design problems with economic and environmental objectives (31, 32, 111, 128, 143, 147). For simple problems involving discrete alternatives and only two objectives, the set of nondominated alternatives may be identified by inspection (145).

The selection of the "best compromise" alternative from the set of nondominated alternatives requires input about the values and preferences of the people responsible for making the decision. Thus, design teams working on a problem with multiple objectives are faced with the need to apply multiattribute decision-making techniques (178, 179), in which most process engineers are not trained. Some authors attempt to avoid the elicitation of values by normalizing the objectives (so that their values for all alternatives are in the range 0–1) and then computing a norm (31, 79, 147). This does not remove the need to evaluate trade-offs; it merely makes it more difficult to do so by eliminating relevant information.

Multiobjective goal programming is a technique that has also been used to solve chemical process design problems without specifying weighting factors to trade off one objective against another (43, 118). The procedure involves stating goals for each objective of the design, ranking the objectives in order of importance, and choosing the alternative that minimizes lexicographically the vector of deviations from the aspiration levels. With this procedure, the decision maker makes trade-offs implicitly by specifying the aspiration levels. In addition, it is likely that the trade-offs will not be consistent across projects because the aspiration levels will be case specific. A further problem with this technique lies in its use of lexicographical minimization, because the technique does not attempt to balance conflicting objectives. An even marginal improvement in a highly ranked goal is preferred to large improvements in goals ranked below. An example of this is given by a lexicographic pollution prevention index that has been used to rank pollution prevention alternatives (71, 72). In this index, the classification of the solution according to the pollution-prevention hierarchy is given priority over all other considerations. As a result, the most expensive, inefficient, and difficult to implement source reduction alternative is ranked higher than the most profitable, effective, and easy to implement recycling option.

Weighted sums of dimensionless scores are commonly used to make decisions involving multiple criteria. In the analytical hierarchy process, the criteria are organized in a hierarchy, where higher level scores are weighted sums of lower level scores (180). Trade-offs made using these methods will not be consistent across projects because the attribute values used in the normalization are case specific. Applications of these techniques to pollution-prevention projects have been published (41, 181, 182).

A different reaction to the valuation problem is to dismiss it as a "social science" problem outside of the field of process engineering, but this gives no assistance to design engineers facing the challenge of making a decision. Our perspective on this issue is that even though it may be difficult to establish precise levels for the trade-offs that decision makers are prepared to make, it is always possible to place bounds on them. Sensitivity analysis (discussed in the next section) can then be used to determine whether there is a need to undertake more thorough elicitation of preferences. Ideally, many of these questions would be addressed at the corporate or division level, allowing management to give design teams uniform guidance regarding the trade-offs the company is prepared to make among the different objectives.

SENSITIVITY ANALYSIS

The main goal of sensitivity analysis is to determine whether the best alternative identified advances the design objectives sufficiently, given current levels of uncertainty, to make further search unnecessary. Framing of the design problem should specify the criteria to be used to determine whether the gains from additional analysis are worth the additional time required. With respect to environmental objectives, the design team needs to be able to identify those aspects of the design that are driving the environmental impact. It is also necessary to understand the trade-offs associated with the modification of the aspects of the design driving the impacts.

Ciric and collaborators have noted that costs associated with waste treatment and disposal are difficult to estimate because direct costs (e.g. landfill fees) are rapidly increasing and indirect costs (e.g. liability, paperwork) are significant but hard to quantify (128, 143). This observation motivated them to develop a procedure for determining the sensitivity of the maximum net profits of a chemical process to changes in the waste treatment cost. In this procedure, the concave portions of the solution set of the multiobjective problem that maximizes profits and minimizes waste are mapped into the solutions of the original profit-maximization problem for different values of the waste-treatment cost.

There are few examples of the application of sensitivity analysis to published mathematical programming formulations of waste minimization (113, 116, 132). Two of these examples examine only the impact of adding additional structural constraints on the network of separation units (116, 132), whereas the other one analyzed the sensitivity of the optimal network to equipment cost (113). Sensitivity analysis on variables fixed at the problem framing stage (e.g. recovery or concentration targets) has not been reported.

Many aspects of the evaluation of a chemical process design with respect to its environmental performance are subject to considerable uncertainty. Diwekar examined the impact of uncertainties associated with technical factors alone (e.g. equipment performance, emission rates) in the economic and environmental performance of a power plant design (151). Proponents of environmental impact assessment indices (163, 171) have noted the need for quantifying the uncertainties in environmental indices and in any rankings that may result from these indices, but work in this area is still in its infancy.

In order to improve the environmental performance of a design, it is necessary to understand which features of a design are the main drivers of its environmental impact. Thus, the calculation of an environmental index is not useful unless the results can be presented in a way that allows the design team to set priorities for further design work. Unfortunately, most of the work reported in the literature has not addressed this problem. Tools analogous to the cost diagrams introduced by Douglas & Woodcock for the screening of designs based on economic objectives (183) could be useful in this regard. Hilaly & Sikdar (77, 78) recommend the calculation of pollution indices (a measure of the mass of waste produced per unit mass of product) for a complete flow sheet as well as for individual process streams. In their procedure, the units associated with process streams with high pollution indices are then targeted for waste minimization. Heinzle & Hungerbühler (187) use a mass loss index (MLI) to allocate all mass flows leaving a process to their cause. Causes of mass inefficiencies include stoichiometric formation of by-products in desired reactions, incomplete conversion, selectivity losses, purification losses, impurities contained in substrates, and losses of solvents, catalysts, and other auxiliary materials not recycled with 100% efficiency. By weighting individual streams by their cost or by a relative measure of environmental impact, those causes of mass inefficiency with the greatest cost or potential ecological impact can be identified. The design team would focus their attention on reducing those sources of inefficiency in the next iteration.

RESEARCH NEEDS

In December of 1992, the Center for Waste Reduction of the American Institute of Chemical Engineers, the US Environmental Protection Agency, and the US Department of Energy sponsored a workshop to identify requirements for improving process simulation and design tools with respect to the incorporation of environmental considerations in the simulation and design of chemical processes (184, 185). Most of the needs identified during that workshop are still present today. The following lists combine the needs identified in that workshop that we find most relevant (marked with an asterisk) with additional needs we identified during the preparation of this review.

Generation of Alternatives

1. Increase the integration of process chemistry into the generation of design alternatives.
2. Develop tools to identify new reaction pathways and catalysts.*
3. Extend alternative generation methods to include nonconventional unit operations.*
4. Develop methods that allow the rapid identification of opportunities to integrate processes.
5. Develop methods to recognize opportunities to match waste streams with feed streams and to prescribe the operations needed to transform a waste stream into a usable feed stream.

Analysis of Alternatives

1. Predict generation of undesired by-products.*
2. Improve prediction of reaction rates.*
3. Predict fugitive emissions and emissions from nonroutine operations (e.g. start-up).*
4. Improve characterization of nonequilibrium phenomena.*
5. Include waste-treatment unit operations in process simulators.
6. Increase the ability of process simulators to track dilute species.*
7. Improve stochastic modeling and optimization.*
8. Link process and environmental models.*

9. Build databases of properties relevant to environmental characterization of processes and link them to process simulators.
10. Include information about uncertainties in databases.
11. Create databases with typical mass and energy balances (including trace components of environmental significance) for widely used raw materials in the chemical industry to facilitate the characterization of upstream processes.
12. Develop guidelines to match the level of detail used in process models with the accuracy needed to make decisions.

Evaluation of Alternatives

1. Develop accounting rules to allocate environmental impacts to specific processes and products in complex plants.
2. Develop environmental impact indices that are able to combine data of different quality while preserving their information content.
3. Develop screening indicators.
4. Develop frameworks that facilitate the elicitation of preferences needed as input to multiobjective optimization.

Sensitivity Analysis

1. Incorporate sensitivity analysis as a standard element in papers and books related to chemical process design.
2. Develop indicator frameworks that allow rapid identification of the features of a design that drive its environmental impact.

CONCLUSIONS

Environmental issues are emerging as one of the major driving forces for change in the chemical industry. This paper has presented a review of the issues, methodologies, and future needs for integrating environmental concerns into the design and operation of chemical manufacturing facilities. Although there are clearly many needs, perhaps one of the most overriding opportunities is for a change in attitudes. A view of product and process design that sees environment as an objective and not just as a constraint on operations can lead to the discovery of design alternatives that improve both environmental and economic performance. An adoption of environmentally conscious design ideas in academic curricula is perhaps the most significant leverage point for moving the practice of chemical process design in this direction.

Literature Cited

1. US Environ. Prot. Agency. 1996. *RCRA Environmental Indicators Progress Report: 1995 Update*. Washington, DC: US Environ. Prot. Agency, Off. Solid Waste
2. US Environ. Prot. Agency. 1997. *1995 Toxic Release Inventory Public Data Release. EPA 745-R-97-005*. Washington, DC: US Environ. Prot. Agency, Off. Pollut. Prev. Toxics
3. Shanley A, Ondrey G, Chaowdury J. 1997. Responsible care gains momentum. *Chem. Eng*. 104:39–41
4. Cascio J, Shideler JC. 1998. Implementing ISO 14001 around the world. *CHEMTECH* 28(5):49–53
5. Sheldon RA. 1997. Catalysis: the key to waste minimization. *J. Chem. Tech. Biotechnol*. 68:381–88
6. Sheldon RA. 1994. Consider the environmental quotient. *CHEMTECH* 24:38–47
7. Chem. Manuf. Assoc. 1997. *The CMA Economic Survey: Outlook for 1997 and Beyond*. Arlington, CA: Chem. Manuf. Assoc.
8. Valle-Riestra JF. 1983. *Project Evaluation in the Chemical Process Industries*. New York: McGraw-Hill. 731 pp.
9. Ulrich GD. 1984. *A Guide to Chemical Engineering Process Design and Economics*. New York: Wiley. 472 pp.
10. Wells GM. 1991. *Handbook of Petrochemicals and Processes*. Aldershot, UK: Gower. 400 pp.
11. Douglas JM. 1988. *Conceptual Design of Chemical Processes*. New York: McGraw-Hill. 601 pp.
12. Edgar TF, Himmelblau DM. 1988. *Optimization of Chemical Processes*. New York: McGraw-Hill. 652 pp.
13. Baasel WD. 1990. *Preliminary Chemical Engineering Plant Design*. New York: Van Nostrand-Reinhold. 572 pp.
14. Hartmann K, Kaplick K. 1990. *Analysis and Synthesis of Chemical Process Systems*. Amsterdam: Elsevier
15. Peters MS, Timmerhaus KD. 1991. *Plant Design and Economics for Chemical Engineers*. New York: McGraw-Hill. 910 pp. 4th ed.
16. Smith R. 1995. *Chemical Process Design*. New York: McGraw-Hill
17. Ludwig EE. 1995. *Applied Process Design for Chemical and Petrochemical Plants*. Houston, TX: Gulf. 3rd ed.
18. Woods DR. 1995. *Process Design and Engineering Practice*. Englewood Cliffs, NJ: Prentice Hall
19. Perry RH, Green DW, Maloney JO, eds. 1997. *Perry's Chemical Engineers' Handbook*. New York: McGraw-Hill. 7th ed.
20. Biegler LT, Grossmann IE, Westerberg AW. 1997. *Systematic Methods of Chemical Process Design*. Upper Saddle River, NJ: Prentice Hall. 796 pp.
21. Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. 1998. *Analysis, Synthesis, and Design of Chemical Processes*. Upper Saddle River, NJ: Prentice Hall. 814 pp.
22. Spriggs HD. 1994. Integration: the key to pollution prevention. *Waste Manage*. 14(3–4):215–29
23. Sinnott RK. 1993. *Chemical Engineering Design. Coulson & Richardson's Chemical Engineering*. Oxford, UK: Pergamon. 954 pp. 2nd ed.
24. Sargent RWH. 1998. A functional approach to process synthesis and its application to distillation systems. *Comput. Chem. Eng*. 22(1–2):31–45
25. DeVito SC, Garrett RL, eds. 1996. *Designing Safer Chemicals: Green Chemistry for Pollution Prevention*. Washington, DC: Am. Chem. Soc. 254 pp.
26. Grossmann IE. 1985. Mixed-integer programming approach for the synthesis of integrated process flowsheets. *Comput. Chem. Eng*. 9(5):463–82
27. Blau GE. 1995. Introduction to green trends in design. *AIChE Symp. Ser*. 91(304):69–71
28. Linnhoff B. 1994. Use pinch analysis to knock down capital costs and emissions. *Chem. Eng. Prog*. 90(8):32–57
29. Mizsey P. 1994. Waste reduction in the

chemical industry: a two level problem. *J. Hazard. Mater.* 37:1–13
30. El-Halwagi MM. 1997. *Pollution Prevention Through Process Integration: Systematic Design Tools*. San Diego, CA: Academic
31. Grossmann IE, Drabbant R, Jain RK. 1982. Incorporating toxicology in the synthesis of industrial chemical complexes. *Chem. Eng. Commun.* 17:151–70
32. Pistikopoulos EN, Stefanis SK, Livingston AG. 1995. A methodology for minimum environmental impact analysis. *AIChE Symp. Ser.* 90(303):139–51
33. Stefanis SK, Livingston AG, Pistikopoulos EN. 1995. Minimizing the environmental impact of process plants: a process systems methodology. *Comput. Chem. Eng.* 19(Suppl.):S39–S44
34. Kniel GE, Delmarco K, Petroe JG. 1996. Life cycle assessment applied to process design: environmental and economic analysis and optimization of a nitric acid plant. *Environ. Prog.* 15(4):221–28
35. Bretz R, Fankhauser P. 1997. Life-cycle assessment of chemical production processes: a tool for ecological optimization. *CHIMIA* 51(5):213–17
36. Smith R, Delaby O. 1991. Targeting flue gas emissions. *Trans. Int. Chem. Eng.* 69A:492–505
37. Gupta A, Manousiouthakis V. 1996. Variable target mass-exchange network synthesis through linear programming. *AIChE J.* 42(5):1326–40
38. Keeney RL. 1992. *Value-Focused Thinking*. Cambridge, MA: Harvard Univ. Press. 416 pp.
39. Kiperstok A, Sharratt PN. 1997. Optimization of pollution control operations in industrial sites considering decay capabilities of the receptors. *Comput. Chem. Eng.* 21(Suppl.):S977–82
40. Sharratt PN, Kiperstok A. 1996. Environmental optimisation of releases from industrial sites into a linear receiving body. *Comput. Chem. Eng.* 20(Suppl.):S1413–18
41. Klee H, Podar MK. 1992. *Project Summary: Yorktown Pollution Prevention Project*. Natl. Tech. Inf. Serv. (NTIS) Doc. No. PB92228527. Chicago, IL: Amoco/Environ. Prot. Agency
42. Lerou JJ, Ng KM. 1996. Chemical reaction engineering: a multiscale approach to a multiobjective task. *Chem. Eng. Sci.* 51(10):1595–614
43. Linninger AA, Ali SA, Stephanopoulos E, Han C, Stephanopoulos G. 1995. Synthesis and assessment of batch processes for pollution prevention. *AIChE Symp. Ser.* 90(303):46–58
44. Anastas PT, Farris CA, eds. 1994. *Benign by Design: Alternative Synthetic Design for Pollution Prevention*. Washington, DC: Am. Chem. Soc. 195 pp.
45. Anastas PT, Williamson TC, eds. 1996. *Green Chemistry: Designing Chemistry for the Environment*. Washington, DC: Am. Chem. Soc. 250 pp.
46. Siirola JJ. 1995. An industrial perspective on process synthesis. *AIChE Symp. Ser.* 91(304):222–33
47. Allen DT, Rosselot KS. 1997. *Pollution Prevention for Chemical Processes*. New York: Wiley
48. Manousiouthakis V, Allen D. 1995. Process synthesis for waste minimization. *AIChE Symp. Ser.* 91(304):72–86
49. Rossiter AP, Kumana JD. 1995. Pollution prevention and process integration: two complementary philosophies. See Ref. 186, pp. 43–49
50. Spriggs HD. 1995. Design for pollution prevention. *AIChE Symp. Ser.* 90(303):1–11
51. Chadha N, Parmele CS. 1993. Minimize emissions of air toxics via process change. *Chem. Eng. Prog.* 89(1):37–42
52. Chadha N. 1994. Develop multimedia pollution prevention strategies. *Chem. Eng. Prog.* 90(11):32–39
53. Goldblatt ME, Eble KS, Feathers JE. 1993. Zero discharge: what, why and how. *Chem. Eng. Prog.* 89(4):22–27
54. Luper D. 1996. Integrate waste minimization into R&D and design. *Chem. Eng. Prog.* 92(6):58–60
55. Haseltine DM. 1992. Wastes: to burn, or not to burn? *Chem. Eng. Prog.* 88(7):53–58
56. Doerr WW. 1996. Use guidewords to identify pollution prevention opportunities. *Chem. Eng. Prog.* 92(8):74–80
57. Zinkus GA, Byers WD, Doerr WW. 1998. Identify appropriate water reclamation technologies. *Chem. Eng. Prog.* 94(5):19–31
58. Bravo JL. 1994. Design steam strippers for water treatment. *Chem. Eng. Prog.* 90(12):56–63
59. Nelson KE. 1990. Use these ideas to cut waste. *Hydrocarbon Process.* 69:93–98
60. Smith R, Petela E. 1991. Waste minimisation in the process industries. Part 1: The problem. *Chem. Eng.* 506:24–25
61. Smith R, Petela E. 1991. Waste minimisation in the process industries. Part 2: Reactors. *Chem. Eng.* 509/510:17–23
62. Smith R, Petela E. 1992. Waste minimisation in the process industries. Part 3:

Separation and recycle systems. *Chem. Eng.* 513:24–28

63. Smith R, Petela E. 1992. Waste minimisation in the process industries. Part 4: Process operations. *Chem. Eng.* 517:21–23
64. Smith R, Petela E. 1992. Waste minimisation in the process industries. Part 5: Utility waste. *Chem. Eng.* 523:32–35
65. Smith R, Petela E, Wang Y. 1994. Water, water everywhere. *Chem. Eng.* 565:21–24
66. Englehardt JD. 1993. Pollution prevention technologies: a review and classification. *J. Hazard. Mater.* 35:119–50
67. US Environ. Prot. Agency. 1995. *Profile of the Inorganic Chemical Industry. EPA 310-R-95-004*. Washington, DC: US Environ. Prot. Agency, Off. Enforc. Compliance Assur.
68. US Environ. Prot. Agency. 1995. *Profile of the Petroleum Refining Industry. EPA 310-R-95-013*. Washington, DC: US Environ. Prot. Agency, Off. Enforc. Compliance Assur.
69. US Environ. Prot. Agency. 1995. *Profile of the Organic Chemicals Industry. EPA 310-R-95-012*. Washington, DC: US Environ. Prot. Agency, Off. Enforc. Compliance Assur.
70. US Environ. Prot. Agency. 1995. *Profile of the Rubber and Plastics Industry. EPA 310-R-95-016*. Washington, DC: US Environ. Prot. Agency, Off. Enforc. Compliance Assur.
71. Smith RL, Khan JA. 1995. Unit operations database for transferring waste minimization solutions. See Ref. 186, pp. 133–48
72. Slater SA, Khan J, Smith RL. 1995. Transferring waste minimization solutions between industrial categories with a unit operations approach: I. Chemical and plating industries. *J. Environ. Sci. Health* A30(2):379–406
73. Shyamkumar C, Jayagopal M, Czekaj CL, High KA. 1995. Process analysis of sulfolane production: a case study in application of process simulation and optimization for waste eduction. *AIChE Symp. Ser.* 91(304):293–96
74. van der Helm DU, High KA. 1996. Waste minimization by process modification. *Environ. Prog.* 15(1):56–61
75. Dantus MM, High KA. 1996. Economic evaluation for the retrofit of chemical processes through waste minimization and process integration. *Ind. Eng. Chem. Res.* 35:4566–78
76. Kürüm S, Heinzle E, Hungerbühler K. 1997. Plant optimisation by retrofitting using a hierarchical method: entrainer selection, recycling and heat integration. *J. Chem. Technol. Biotechnol.* 70:29–44
77. Hilaly AK, Sikdar SK. 1994. Pollution balance: a new methodology for minimizing waste production in manufacturing processes. *J. Air Waste Manage. Assoc.* 44(11):1303–8
78. Hilaly AK, Sikdar SH. 1995. Pollution balance method and the demonstration of its application to minimizing waste in a biochemical process. *Ind. Eng. Chem. Res.* 34:2051–59
79. Cabezas H, Bare JC, Mallick SK. 1997. Pollution prevention with chemical process simulators: the generalized waste reduction (WAR) algorithm. *Comput. Chem. Eng.* 21(Suppl.):S305–10
80. Mallick SK, Cabezas H, Bare JC, Sidkar SK. 1996. A pollution reduction methodology for chemical process simulators. *Ind. Eng. Chem. Res.* 35:4128–38
81. Hopper JR, Yaws CL, Vichailak M, Ho TC. 1994. Pollution prevention by process modification: reactions and separations. *Waste Manage.* 14(3–4):187–202
82. Hopper JR, Yaws CL, Ho TC, Vichailak M. 1993. Waste minimization by process modification. *Waste Manage.* 13(1):3–14
83. Hopper JR, Yaws CL, Ho TC, Vichailak M, Muninnimit A. 1992. Waste minimization by process modification. In *Industrial Environmental Chemistry,* ed. DT Sawyer, AE Martell, pp. 25–43. New York: Plenum
84. Douglas JM. 1992. Process synthesis for waste minimization. *Ind. Eng. Chem. Res.* 31:238–43
85. Fonyo Z, Kürüm S, Rippin DWT. 1994. Process development for waste minimization: the retrofitting problem. *Comput. Chem. Eng.* 18(Suppl.):S591–95
86. Rossiter AP, Spriggs HD, Howard Klee J. 1993. Apply process integration to waste minimization. *Chem. Eng. Prog.* 89(1):30–36
87. Douglas JM. 1995. Synthesis of separation system flowsheets. *AIChE J.* 41(12):2522–36
88. Buehner FW, Rossiter AP. 1996. Minimize waste by managing process design. *CHEMTECH* 26:64–72
89. Smith R, Petela EA, Spriggs HD. 1990. Minimization of environmental emissions through improved process integration. *Heat Recovery Syst. Comb. Heat Power* 10(4):329–39
90. Körner H. 1988. Optimaler Energieeinsatz in der Chemischen Industrie. *Chem. Ing. Tech.* 60(7):511–18
91. Richburg A, El-Halwagi MM. 1995. A

graphical approach to the optimal design of heat-induced separation networks for VOC recovery. *AIChE Symp. Ser.* 91(304):256–59

92. El-Halwagi MM. 1989. Synthesis of mass exchange networks. *AIChE J.* 35(8): 1233–44
93. El-Halwagi MM, Hamad AA, Garrison GW. 1996. Synthesis of waste interception and allocation networks. *AIChE J.* 42(11):3087–101
94. Wang YP, Smith R. 1995. Wastewater minimization with flowrate constraints. *Trans. Int. Chem. Eng.* 73A:889–904
95. Wang YP, Smith R. 1994. Wastewater minimization. *Chem. Eng. Sci.* 49(7):981– 1006
96. Wang Y-P, Smith R. 1995. Time pinch analysis. *Trans. Int. Chem. Eng.* 73A: 905–14
97. Wang Y-P, Smith R. 1994. Design of distributed effluent treatment systems. *Chem. Eng. Sci.* 49(18):3127–45
98. Dhole VR, Ramchandani N, Tainsh RA, Wasilewski M. 1996. Make your process water pay for itself. *Chem. Eng.* 103(1):100–3
99. Tripathi P. 1996. Pinch technology reduces wastewater. *Chem. Eng.* 103(11): 87–90
100. Peters J. 1995. TCE excellence in safety and environment awards. *Chem. Eng.* 589:S4
101. Hamilton R, Dowson D. 1994. Pinch cleans up. *Chem. Eng.* 566:42–44
102. Flower JR, Bikos SC, Johnson SW. 1995. A modular approach to synthesis of cleaner processes. *Comput. Chem. Eng.* 19(Suppl.):S45–S50
103. Flower JR, Bikos SC, Johnson SW. 1993. A new graphical method for choosing better mass flowsheets for environmentally aware processes. *Int. Chem. Eng. Symp. Ser.* 132:109–21
104. Ahmad BS, Barton PI. 1995. Solvent recovery targeting for pollution prevention in pharmaceutical and specialty chemical manufacturing. *AIChE Symp. Ser.* 90(303):59–71
105. Joback KG. 1995. Solvent substitution for pollution prevention. *AIChE Symp. Ser.* 90(303):98–104
106. Constantinou L, Jaksland C, Bagherpour K, Gani R, Bogle IDL. 1995. Application of the group contribution approach to tackle environmentally related problems. *AIChE Symp. Ser.* 90(303):105–16
107. Stefanis SK, Buxton A, Livingston AG, Pistikopoulos EN. 1996. A methodolody for environmental impact minimization: solvent design and reaction path synthesis issues. *Comput. Chem. Eng.* 20(Suppl.):S1419–24
108. Duvedi A, Achenie LEK. 1997. On the design of environmentally benign refrigerant mixtures: a mathematical programming approach. *Comput. Chem. Eng.* 21(8):915–23
109. Knight JP. 1994. *Computer-aided design tools to link chemistry and design in process development*. PhD thesis. MIT, Boston. 518 pp.
110. Crabtree EW, El-Halwagi MM. 1995. Synthesis of environmentally acceptable reactions. *AIChE Symp. Ser.* 90(303): 117–27
111. Lakshmanan A, Biegler LT. 1995. Reactor network targeting for waste minimization. *AIChE Symp. Ser.* 90(303):139–51
112. El-Halwagi MM, Srinivas BK, Dunn RF. 1995. Synthesis of optimal heat-induced separation networks. *Chem. Eng. Sci.* 50(1):81–97
113. El-Halwagi MM. 1993. Optimal design of membrane-hybrid systems for waste reduction. *Sep. Sci. Technol.* 28(1–3):283–307
114. El-Halwagi MM. 1992. Synthesis of reverse-osmosis networks for waste reduction. *AIChE J.* 38(8):1185–98
115. Dunn RF, Zhu M, Srinivas BK, El-Halwagi MM. 1995. Optimal design of energy-induced separation networks for VOC recovery. *AIChE Symp. Ser.* 90(303):74–85
116. Dunn RF, El-Halwagi MM. 1994. Optimal design of multicomponent VOC condensation systems. *J. Hazard. Mater.* 28:187–206
117. Dunn RF, El-Halwagi MM. 1994. Selection of optimal VOC-condensation systems. *Waste Manage.* 14(2):103–13
118. Chang C-T, Hwang J-R. 1996. A multiobjective programming approach to waste minimization in the utility systems of chemical processes. *Chem. Eng. Sci.* 51(16):3951–65
119. El-Halwagi MM, Manousiouthakis V. 1990. Automatic synthesis of mass-exchange networks with single-component targers. *Chem. Eng. Sci.* 45(9):2813–31
120. El-Halwagi MM, Manousiouthakis V. 1990. Simultaneous synthesis of mass-exchange and regeneration networks. *AIChE J.* 36(8):1209–19
121. El-Halwagi MM, Srinivas BK. 1992. Synthesis of reactive mass-exchange networks. *Chem. Eng. Sci.* 47(8):2113–19
122. Srinivas BK, El-Halwagi MM. 1994. Synthesis of reactive mass-exchange networks with general nonlinear equilibrium functions. *AIChE J.* 40(3):463–72

123. Srinivas BK, El-Halwagi MM. 1994. Synthesis of combined heat and reactive mass-exchange networks. *Chem. Eng. Sci.* 49(13):2059–74
124. Papalexandri KP, Pistikopoulos EN, Floudas A. 1994. Mass exchange networks for waste minimization: a simultaneous approach. *Trans. Int. Chem. Eng.* 72A:279–94
125. Gupta A, Manousiouthakis V. 1994. Waste reduction through multicomponent mass exchange network synthesis. *Comput. Chem. Eng.* 18(Suppl.):S585–90
126. Huang YL, Edgar TF. 1995. Knowledge-based design approach for the simultaneous minimization of waste generation and energy consumption in a petroleoum refinery. See Ref. 186, pp. 181–96
127. Friedler F, Varga JB, Fan LT. 1995. Algorithmic approach to the integration of total flowsheet synthesis and waste minimization. *AIChE Symp. Ser.* 90(303):86–97
128. Ciric AR, Huchette SG. 1993. Multiobjective optimization approach to sensitivity analysis: waste treatment costs in discrete process synthesis and optimization problems. *Ind. Eng. Chem. Res.* 32:2636–46
129. El-Halwagi MM, El-Halwagi AM, Manousiathakis V. 1992. Optimal design of dephenolization networks for petroleum-refinery wastes. *Trans. Int. Chem. Eng.* 70B(8):131–39
130. Huang YL, Fan LT. 1994. HIDEN: a hybrid intelligent system for synthesizing highly controllable exchanger networks. Implementation of a distributed strategy for integrating process design and control. *Ind. Eng. Chem. Res.* 33:1174–87
131. Zhu M, El-Halwagi MM. 1995. Synthesis of flexible mass-exchange networks. *Chem. Eng. Commun.* 138:193–211
132. Srinivas BK, El-Halwagi MM. 1993. Optimal design of pervaporation systems for waste reduction. *Comput. Chem. Eng.* 17(10):957–70
133. Edgar TF, Huang YL. 1993. Artificial intelligence approach to synthesis of a process for waste minimization. *Am. Chem. Soc. Symp. Ser.* 554:97–113
134. Anastas PT, Nies JD, DeVito SC. 1994. Computer-assisted alternative synthetic design for pollution prevention at the U.S. Environmental Protection Agency. See Ref. 44, pp. 156–84
135. Hendrickson JB. 1996. Teaching alternative synthesis: the SYNGEN program. In *Green Chemistry: Designing Chemistry for the Environment*, ed. PT Anastas, TC Williamson, pp. 214–31. Washington, DC: Am. Chem. Soc.
136. Petrides DP, Abeliotis KG, Mallick SK. 1994. EnviroCAD: a design tool for efficient synthesis and evaluation of integrated waste recovery, treatment and disposal processes. *Comput. Chem. Eng.* 18(Suppl.):S603–7
137. Linninger AA, Stephanopoulos E, Ali SA, Han C, Stephanopoulos G. 1995. Generation and assessment of batch processes with ecological considerations. *Comput. Chem. Eng.* 19(Suppl.):S7–S13
138. Linninger AA, Ali SA, Stephanopoulos G. 1996. Knowledge-based validation and waste management of batch pharmaceutical process designs. *Comput. Chem. Eng.* 20(Suppl.):S1431–36
139. Schaich JR. 1991. Estimate fugitive emissions from process equipment. *Chem. Eng. Prog.* 87(8):31–35
140. Hertz DW. 1995. Managing the design process. See Ref. 186, pp. 265–87
141. Farag IH, Chen C-C, Wu P-c, Rosen JB. 1992. Modeling pollution prevention. *CHEMTECH* 22:54–61
142. Milne GWA, Wang S, Fung V. 1996. Use of computers in toxicology and chemical design. In *Designing Safer Chemicals: Green Chemistry for Pollution Prevention*, ed. SC DeVito, RL Garrett, pp. 138–55. Washington, DC: Am. Chem. Soc.
143. Ciric AR, Jia T. 1994. Economic sensitivity analysis of waste treatment costs in source reduction projects: continuous optimization problems. *Comput. Chem. Eng.* 18(6):481–95
144. Diwekar UM, Frey HC, Rubin ES. 1992. Synthesizing optimal flowsheets: applications to IGCC system environmental control. *Ind. Eng. Chem. Res.* 31(8):1927–36
145. Rossiter AP, Kumana JD. 1994. Rank pollution prevention and control options. *Chem. Eng. Prog.* 90(2):39–44
146. Papalexandri KP, Pistikopoulos EN. 1996. Generalized modular representation framework for process synthesis. *AIChE J.* 42(4):1010–32
147. Fathi-Afshar S, Yang J-C. 1985. Designing the optimal structure of the petrochemical industry for minimum cost and least gross toxicity of chemical production. *Chem. Eng. Sci.* 40(5):781–97
148. Freeman H, Harten T, Springer J, Randall P, Curran MA, Stone K. 1992. Industrial pollution prevention: a critical review. *J. Air Waste Manage. Assoc.* 42(5):618–56
149. Allen DT. 1992. Industrial pollution prevention: critical review discussion papers. *J. Air Waste Manage. Assoc.* 42(9): 1159–61

150. Lenox M, Ehrenfeld JR. 1995. Design for the environment: a new framework for strategic decisions. *Total Qual. Environ. Manage.* Summer:37–51
151. Diwekar UM. 1995. A process analysis approach to pollution prevention. *AIChE Symp. Ser.* 90(303):168–79
152. Cohen Hubal EA, Overcash MR. 1993. Net waste reduction analysis applied to air pollution control technologies. *Air Waste* 43:1449–54
153. Glauser M, Müller P. 1997. Eco-efficiency: a prerequisite for future success. *CHIMIA* 51(5):201–6
154. Hendershot DC. 1997. Measuring inherent safety, health and environmental characteristics early in process development. *Process Saf. Prog.* 16(2):78–79
155. Laing IG. 1992. Waste minimization: the role of process development. *Chem. Ind.* (18):682–86
156. Benforado DM, Ridlehoover G, Gores MD. 1991. Pollution prevention: one firm's experience. *Chem. Eng.* 98:130–33
157. Klee H. 1992. Industrial pollution prevention: critical review discussion paper. *J. Air Waste Manage. Assoc.* 42(9):1163–66
158. Mak C-P, Mühle H, Achini R. 1997. Integrated solutions to environmental protection in process R&D. *CHIMIA* 51(5):184–88
159. Stephan DG, Knodel RM, Bridges JS. 1994. A "Mark I" measurement methodology for pollution prevention progress occurring as a result of product design decisions. *Environ. Prog.* 13(4):232–46
160. Ahearn J, Fatkin H, Schwalm W. 1991. Polaroid corporation's systematic approach to waste minimization. *Pollut. Prev. Rev.* Summer:257–71
161. Houghton JT, Filho LGM, Callander BA, Harris N, Kattenberg A, Maskell K, eds. 1996. *Climate Change 1995: The Science of Climate Change*. Cambridge, UK: Cambridge Univ. Press
162. ACGIH. 1997. 1997 Threshold limit values for chemical substances in the work environment. *Am. Conf. Gov. Ind. Hyg., Cincinnati, OH*
163. Horvath A, Hendrickson CT, Lave LB, McMichael FC, Wu T-S. 1995. Toxic emissions indices for green design and inventory. *Environ. Sci. Technol.* 29(2):86–90A
164. Davis GA, Swanson M, Jones S. 1994. *Comparative Evaluation of Chemical Ranking and Scoring Methodologies. EPA Order No. 3N-3545-NAEX.* Knoxville, TN: Univ. Tenn., Cent. Clean Prod. Clean Technol.
165. Richner P, Weidenhaupt A. 1997. Environmental risk assessment of chemical susbstances. *CHIMIA* 51(5):222–27
166. Weidenhaupt A, Hungerbühler K. 1997. Integrated product design in chemical industry. A plea for adequate life-cycle screening indicators. *CHIMIA* 51(5):217–21
167. Cave SR, Edwards DW. 1997. Chemical process route selection based on assessment of inherent environmental hazard. *Comput. Chem. Eng.* 21(Suppl.):S965–70
168. US Environ. Prot. Agency. 1997. *Waste Minimization Prioritization Tool User's Guide and system Documentation. EPA 530-R-97-019 (Draft).* Washington, DC: US Environ. Prot. Agency, Off. Pollut. Prev. Toxics
169. Siljeholm J. 1997. A hazard ranking of organic contaminants in refinery effluents. *Toxicol. Ind. Health* 13(4):527–51
170. Hertwich EG, Pease WS, McKone TE. 1998. Evakuating toxic impact assessment methods: What works best? *Environ. Sci. Technol.* 32(5):A138–A44
171. Jia CQ, Di Guardo A, Mackay D. 1996. Toxics release inventories: opportunities for improved presentation and interpretation. *Environ. Sci. Technol.* 30(2):A86–A91
172. Elliott AD, Sowerby B, Crittenden BD. 1996. Quantitative environmental impact analysis for clean design. *Comput. Chem. Eng.* 20(Suppl.):S1377–82
173. Goedkoop M. 1995. *The Eco-Indicator 95: Weighting Method for Environmental Effects that Damage Ecosystems or Human Health on a European Scale.* NOH Rep. 9523. Amersfoort, Netherlands: Novem/RIVM/NOH/PRé Consult.
174. DeSimone LD, Popoff F. 1997. *Eco-Efficiency: The Business Link to Sustainable Development.* Cambridge, MA: MIT Press
175. Berger SA. 1995. The pollution prevention hierarchy as an R&D management tool. *AIChE Symp. Ser.* 90(303):23–28
176. Wright M, Allen D, Clift R, Sas H. 1998. Measuring corporate environmental performance: the ICI environmental burden system. *J. Ind. Ecol.* 1(4):117–27
177. Ahbe S, Braunschweig A, Müller-Wenk R. 1990. *Methodik für Ökobilanzen aufder Basis ökologischer Optimierung.* Schriftenreihe Umwelt Nr. 133. Bern, Switzerland: Swiss Bundes. Umwelt, Wald Landschaft
178. Clemen RT. 1995. *Making Hard Decisions: An Introduction to Decision Analysis.* Belmont, CA: Duxbury. 664 pp. 2nd ed.
179. Keeney RL, Raiffa H. 1993. *Decisions*

With Multiple Objectives: Preferences and Value Tradeoffs. Cambridge, UK: Cambridge Univ. Press. 569 pp.

180. Saaty TL. 1996. *The Analytical Hierarchy Process: Planning, Priority Setting, Resource Allocation*. Pittsburgh, PA: RWS Publ. 287 pp. 2nd ed.
181. Balik JA, Koraido SM. 1991. Identifying pollution prevention options for a petroleoum refinery. *Pollut. Prev. Rev.* 1:273–93
182. Reid RA, Christensen DC. 1994. Evaluate decision criteria systematically. *Chem. Eng. Prog.* 90(7):44–49
183. Douglas JM, Woodcock DC. 1985. Cost diagrams and the quick screening of process alternatives. *Ind. Eng. Chem. Process. Design Dev.* 24(4):970–76
184. Eisenhauer J, McQueen S. 1993. *Environmental Considerations in Process Design and Simulation*. New York: Am. Inst. Chem. Eng.
185. Hilaly AK, Sikdar SK. 1996. Process simulation tools for pollution prevention. *Chem. Eng.* 103:98–105
186. Rossiter AP, ed. 1995. *Waste minimization through process design*. New York: McGraw-Hill
187. Heinzle E, Hungerbühler K. 1997. Integrated Process Development: The Key to Future Production of Chemicals. *CHIMIA* 51(5):176–83