Perspective

# Green Engineering: Environmentally Conscious Design of Chemical Processes and Products


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## Introduction

It is impossible to imagine modern life without the products provided by the chemical industry. Chemical processes provide a vast array of products and materials used in health care, consumer products, transportation, food processing, electronic materials, and construction. Yet, these same chemical processes that provide products essential for modern economies also generate substantial quantities of wastes and emissions. Recent national scale inventories of wastes and emissions indicate that advanced industrialized economies utilize 40–80 ton of material per year, per capita (Adriaanse et al., 1997); the majority of these materials are used once and then discarded.

Since most material use and material displacement are associated with the extraction, production and use of commodity materials, these material flows provide both challenges and opportunities for chemical engineers. The challenge is to keep the costs of chemical products (particularly commodity products) affordable, while continuing to reduce environmental impacts. The opportunities will come from rethinking the approach to meeting environmental goals. Rather than using traditional, end-of-pipe approaches to environmental management, approaches that avoid the generation of wastes or pollutants, variously known as green engineering, environmentally conscious manufacturing, ecoefficient production, or pollution prevention, can provide alternatives that are cost-effective and result in significant environmental improvements.

These general ideas have been receiving increasing attention in the chemical engineering research community for more than a decade, and a number of educational institutions are offering chemical engineering courses and even specializations in pollution prevention or green engineering. But, there remain challenging questions. What constitutes green engineering? What are the tools that a chemical engineer must master to design chemical processes and products that will meet the environmental constraints and goals of the 21st century?

It can be argued that green engineering is simply good chemical engineering. Previous "Perspectives" published in the *Journal* have noted the role of green engineering in process engineering (Grossmann and Westerberg, 2000; Harold and Ogunnaike, 2000), and chemical engineers have worked for decades to design processes that are energy- and mass-efficient. The viewpoint advanced here, however, is that chemical engineers will require a *new group of tools* to address the challenges of green engineering and that these tools can fall into three categories: assessment, improvement, and integration.

## Assessing the Environmental Performance of Chemical Processes and Products

What constitutes a green process or a green product? Early attempts to identify green products focused on the development of ecolabels, such as those shown in Figure 1. Generally administered by governments, these labels attempted to condense complex, multiattribute environmental footprints of products into a single logo (U.S. EPA, 1993; Allen et al., 1998). Either a product was green and could display an eco-label, or it was not. Unfortunately, true environmental performance is rarely so simple. Products and the processes used to manufacture them consume energy, utilize nonrenewable and renewable materials, and generate emissions. In creating designs, product and process engineers are continually forced to make decisions that involve trade-offs between multiple environmental impacts. Consider, for example, the chemical process designer trying to determine whether to use indirect or direct contact heating in a process application. The direct contact heating (e.g., steam injection) may be more energy-efficient than the use of a heat exchanger, but generates a wastewater stream. Alternatively, consider the dilemma of a product designer trying to select a material for an automotive bumper. Should the designer select a steel bumper that is easily recycled or a lightweight polymer composite that leads to better fuel economy?

Such trade-offs are unavoidable. Every product and process will generate an environmental footprint, and only rarely will one design alternative be unambiguously environmentally preferable. Designers will continually face trade-offs between different environmental impacts, yet must ultimately make decisions. Further, designers must reconcile environmental performance with cost and other criteria. Informing these decisions will require a new set of tools that chemical engineers will need to master. In addition, the tools must be robust enough to be used at a variety of decision points in process and product design. The chemical engineer, evaluating hundreds of design alternatives for a process in its initial development stages will need more streamlined tools than the engineer performing a process modification on an existing facility.

For chemical engineers, key groups of environmental assessment tools are beginning to emerge. The tools deal with two distinct issues: 1. how to assess potential environmental impacts at a variety of stages during process design; 2. how to reconcile environmental impacts with other decision criteria.

*Assessing Environmental Impacts.* While detailed environmental impact assessments have been performed for decades, their implementation has generally been restricted to evaluations of completed designs. This severely restricts the range of options that can be considered to improve environmental performance. A better approach would be to evaluate environmental performance at each step in the design process. Consider how this might be implemented in a typical process design. At the earliest stages of a process design, only the most elementary data on raw materials, products and by-products of a chemical process may be available, and large numbers of design alternatives may need to be considered. Yet, despite the availability of only limited information, there is a need to identify potentially hazardous process materials, consider alternative reaction pathways, and identify key emission points in the process. Chemical engineers need tools that will allow them to quickly assess the potential environmental persistence, bioaccumulation potential, and toxicity of new chemical products and intermediates. They also need tools that will allow key compounds of concern or emission points in chemical processes to be identified. Table 1 provides a simple example of the type of assessment that chemical engineers will need to perform with limited information.


**Figure 1. Eco-labels from around the world.**
Generally administered by governments, these labels attempt to condense complex, multi-attribute environmental footprints of products into a single logo.

Table 1 shows two alternative synthesis routes for the production of methyl methacrylate and demonstrates how they can be quickly evaluated to assess potential environmental concerns. The data in Table 1 can be estimated using group contribution methods when measurements are not available; the estimates of persistence, bioaccumulation, toxicity and stoichiometry can then be combined to provide preliminary guidance (Allen and Shonnard, 2001). In this case, the concerns are dominated by the health and safety issues associated with sulfuric acid, and the isobutlyene route appears preferable because it requires less acid. Although more detailed data are available for these two processes, this level of data is typical of what might be available for new process chemistries.

Once the basic structure of a process has been designed, the engineer will be able to perform more detailed environmental evaluations, but will face another level of design decisions that will influence environmental performance. Figure 2 provides an example of the type of decision that a process designer would face. In this simple example, absorption with a regenerable solvent is used to capture (and recycle or sell) toluene and ethyl acetate, which might otherwise be emitted into the atmosphere. To increase the fraction of the hydrocarbons absorbed, the circulation rate of the solvent can be increased, but this will increase the duties of the reboiler, condenser and pumps in the system, increasing energy use and atmospheric emissions—primarily of criteria pollutants (sulfur and nitrogen oxides, particulates, and carbon monoxide), and of the greenhouse gas $CO_2$. The process engineer will need emission estimation tools to evaluate such trade-offs, and will need to evaluate the potential environmental and economic costs associated with different types of emissions—in this example the relative costs of hydrocarbon emissions as opposed to emissions of criteria pollutants and $CO_2$.

*Assessing Environmental Costs.* A second type of environmental assessment tool will allow the chemical process designer to reconcile environmental impacts with other decision criteria. Since evaluation of costs is the primary mechanism for business decision-making, significant efforts have been made to quantify environmental costs and benefits. The most relevant work for the design of chemical processes has been done by the American Institute of Chemical Engineers' Center for Waste Reduction Technologies (AIChE–CWRT, 2000). The CWRT Total Cost Assessment (TCA) methods identify five tiers of environmental costs.

Tier I: costs normally captured by engineering economic evaluations

Tier II: administrative and regulatory environmental costs not normally assigned to individual projects

Tier III: liability costs

Tier IV: costs and benefits, internal to a company, associated with improved environmental performance

Tier V: costs and benefits, external to a company, associated with improved environmental performance

Tier I costs are the types of costs quantified in traditional economic analyses. Traditional accounting systems that focus on Tier I costs often charge some types of environmental costs to overhead, and these costs may therefore be "hidden" during project cost evaluations. These are referred to as Tier II or hidden costs. A less tangible set of costs are those designated as Tier III—liability costs. Liability costs could include compliance obligations, remediation obligations, fines and penalties, obligations to compensate for private parties, punitive damages, and natural resource damages. A final set of costs are designated as Tier IV or V, which can be referred to as image or relationship costs (AIChE–CWRT, 2000). These costs arise in relationships with customers, investors, insurers, suppliers, lenders, employees, regulators, and communities. They are perhaps the most difficult to quantify.

Thus, a basic framework for estimating costs and benefits associated with environmental activities consists of five tiers, beginning with the most tangible costs and extending to the least quantifiable costs. Tier I costs, by definition, are captured effectively by conventional accounting methods. Tier II costs are certain, yet are often difficult to separate from general overhead expenditures. Estimating Tier III-V costs poses different challenges. These costs are, in many cases, due to unplanned events, such as incidents that result in civil fines, remediation costs or other charges. While these events are not planned, they do occur. Therefore, it is prudent to estimate the expected value of these costs. Arriving at an expected value for Tier III-V costs involves estimating the probability that an event will occur, the costs associated with the event, and when the event will occur. For example, if the goal is to estimate the expected value of a civil fine or penalty (a Tier III cost), the likelihood that a fine will be assessed and the likely magnitude of that fine must be calculated. If the probability of a fine being assessed is 0.1 (1 chance in 10) per year and the likely magnitude of the fine is $10,000, the expected annual cost due to fines would be $1,000. For events that will occur in future years, such as costs of complying with anticipated future regulations, knowledge of when the event will occur is critical to determining the present value of the expected costs.

*Summary of Environmental Assessment Tools.* A robust set of environmental impact and cost assessment tools, designed specifically for chemical processes are beginning to emerge. These tools are currently in their initial development stages and much work remains to be done in taking them from directional indicators of performance to quantitative environmental impact and cost evaluation tools. Nevertheless, the evaluation frameworks are beginning to take shape and the next generation of chemical engineers can expect to integrate the evaluation of environmental objectives into every phase of the design process.

**Table 1. Stoichiometric, Persistence, Toxicity and Bioaccumulation Data for Two Synthesis Routes for Methyl Methacrylate**

| Compound | lb(kg) Produced or Required per lb(kg) of Methyl Methacrylate* | Atmospheric Half-Life/Aquatic Half-Life** | 1/TLV† $(ppm)^{-1}$ | Bioconc. Factor‡ (Conc. in Lipids/Conc. in Water) |
|---|---|---|---|---|
| *Acetone-cyanohydrin route* | | | | |
| Acetone | –0.68 (–0.31) | 52 d/wk | 1/750 | 3.2 |
| Hydrogen cyanide | –0.32 (–0.15) | 1 yr/wk | 1/10 | 3.2 |
| Methanol | –0.37 (–0.168) | 17 d/d | 1/200 | 3.2 |
| Sulfuric acid*** | –1.63 (–0.74) | | 1/2 (est.) | |
| Methyl methacrylate | 1.00 (0.45) | 7 h/wk | 1/100 | 2.3 |
| *Isobutylene route* | | | | |
| Isobutylene | –1.12 (–0.51) | 2.5 h/wk | 1/200 (est.) | 12.6 |
| Methanol | –0.38 (–0.172) | 17 d/d | 1/200 | 3.2 |
| Pentane | –0.03 (–0.014) | 2.6 d/d | 1/600 | 81 |
| Sulfuric acid*** | –0.01 (–0.005) | | 1/2 (est.) | |
| Methyl methacrylate | 1.00 (0.45) | 7 h/wk | 1/100 | 2.3 |

*A negative stoichiometric index indicates that a material is consumed; a positive index indicates that it is produced in the reaction.
**The atmospheric half-life is based on the reaction with the hydroxyl radical; aquatic half-life via biodegradation is based on expert estimates.
***The lifetime of sulfuric acid in the atmosphere is short due to reactions with ammonia.
†TLV is the threshold limit value, and the inverse is a measure of inhalation toxicity potential for a chemical.
‡Bioconcentration factor is an indicator of a chemical's potential to accumulate through the food chain.

## Improving Environmental Performance of Chemical Processes and Products

Once a set of tools is available for assessing environmental impacts and costs, chemical engineers can apply traditional analysis and design methods to improve mass efficiency, energy efficiency, and environmental performance. Advances in catalysis, reaction engineering, separations, process synthesis, process control, and other areas can all make contributions. But, are there tools and skills that will need to be developed specifically to im-prove environmental performance? Our perspective is that a few such tools will emerge. They might include better methods for modeling very dilute solutions (since pollutants are generally present at very low concentrations) at process conditions and the ability to predict the yields of trace byproducts under process reaction conditions. On balance, however, the tools for improving environmental performance will be the same as the tools that chemical engineers have worked for decades to master.

## Moving Beyond Plant Boundary: Integrating Process Design with Supply Chain Management and Product Stewardship

While it is appropriate for chemical engineers to focus on evaluating and improving the environmental performance of chemical processes, it is also important to recognize that chemical manufacturing processes are linked to both suppliers and customers. Customers will be concerned about the environmental performance of chemical products that they use, and so process design engineers must increasingly become stewards for their products. In addition, chemical processes are linked to their suppliers, so engineers must be aware of the linkages between their processes and other chemical processes and other industrial sectors.

*Product and Process Stewardship.* Life cycle assessment (LCA) has become an important part of environmental product and process stewardship. The tools of life cycle assessment recognize that products, services, and processes all have a life cycle. For products, the life cycle begins when raw materials are extracted or harvested. Raw materials then go through a number of manufacturing steps until the product is delivered to a customer. The product is used, then disposed of or recycled. Figure 3 shows these product life cycle stages along the horizontal axis, as well as energy consumption and wastes and emissions generated in all of these life cycle stages.

Processes also have a life cycle. The life cycle begins with planning, research and development. The products and processes are then designed and constructed. A process will have an active lifetime, then will be decommissioned, and, if necessary, remediation and restoration may occur. Figure 3, along its vertical axis, illustrates the main elements of this process life cycle. Again, energy consumption, wastes, and emissions are associated with each step in the life cycle.

Traditionally, product designers have been concerned primarily with product life cycles up to and including the manufacturing step. Chemical process designers have been concerned primarily with process life cycles up to and including the manufacturing step. That focus is changing. Increasingly, chemical product designers must consider how their products will be recycled. They must consider how their customers will use their products and what environmental hazards might arise. Process designers must avoid contamination of the sites at which their processes are located. Simply stated, engineers must become stewards for their products and processes throughout their life cycles. An introduction to this emerging area is provided by Allen and Shonnard (2001).

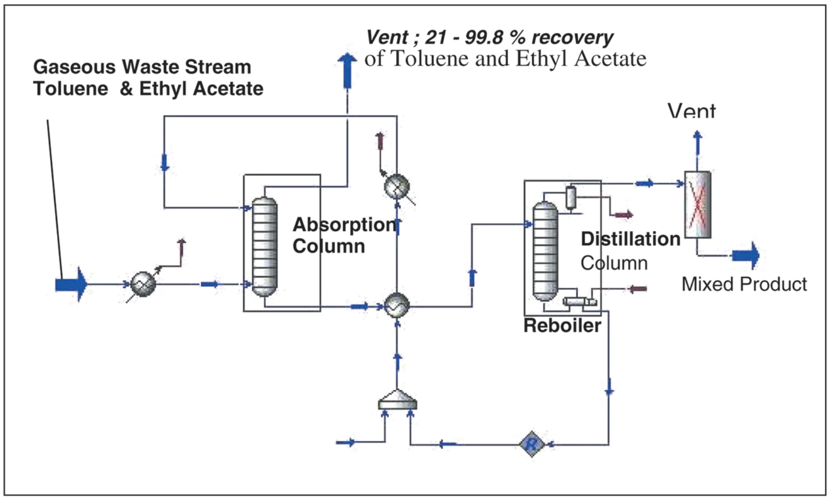


**Figure 2. Absorption with a regenerable solvent is used to capture toluene and ethyl acetate, which might otherwise be emitted into the atmosphere.** To increase the fraction of the hydrocarbons absorbed, the circulation rate of the solvent can be increased, but it will increase energy use and atmospheric emissions of criteria pollutants. The process engineer will need emission estimation tools to evaluate the potential environmental and economic costs associated with different types of emissions. (Adapted from Allen and Shonnard, 2001)

*Integrating Material and Energy Flows along Supply Chains: Industrial Ecology.* Chemical processes do not operate in isolation. The products and byproducts of one process serve as raw materials for other chemical processes. To understand how the environmental performance of a chemical process is governed not only by the design of the process, but also by how the process integrates with other processes and material flows, consider a classic example—the manufacture of vinyl chloride.

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

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

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

In this synthesis route, 1 mol of hydrochloric acid is produced for every mol of vinyl chloride. Considered in isolation, this process might be considered wasteful. Half of the original chlorine winds up, not in the desired product, but in a waste acid. The process, however, is not operated in isolation. The waste hydrochloric acid from the direct chlorination of ethylene can be used as a raw material in the oxychlorination of ethylene. In this process, hydrochloric acid, ethylene, and oxygen are used to manufacture vinyl chloride:

$$HCl + H_2C{=}CH_2 + 0.5\ O_2 \rightarrow H_2C{=}CHCl + H_2O$$

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

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

$$CO + Cl_2 \rightarrow COCl_2$$

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

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

The isocyanate is subsequently used in urethane production, and the hydrochloric acid is recycled. The key feature of the isocyanate process chemistry is that chlorine does not appear in the final product. Thus, chlorine can be processed through the system without being consumed. It may be transformed from molecular chlorine to hydrochloric acid, but the chlorine is still available for incorporation into final products, such as vinyl chloride, that contain chlorine. A chlorine-hydrogen chloride network incorporating both isocyanate and vinyl chloride has been developed in the U.S. Gulf Coast.

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

Finding productive uses for byproducts is a principle that has been used for decades in chemical manufacturing. What is relatively new, however, is the search for chemical byproduct uses in industries that extend far beyond chemical manufacturing. Chemical engineers should take on design tasks such as managing the heat integration between a power plant and an oil refinery, or integrating water use between semiconductor and commodity chemical manufacturing. Such design tasks are currently at the brink of our design abilities. To make these design tasks as common in the next decades as heat integration within a process, we will need to broaden our perspectives. We must begin to integrate process design tools from fields ranging from chemical manufacturing to semiconductor manufacturing, as well as from pulp and paper processing to polymer recycling.

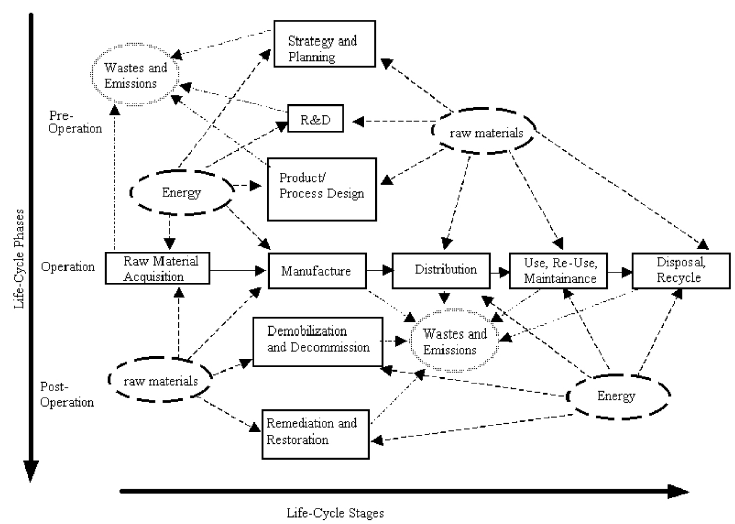


**Figure 3 Product life cycles including raw material extraction, material processing, use and disposal steps, as shown along the horizontal axis.**
Process life cycles include planning, research, design, operation, and decommissioning steps as shown along the vertical axis. In both product and process life cycles, energy and materials are used at each stage of the life cycle, and emissions and wastes are created.

## Summary

Preliminary engineering design tools for assessing, improving, and integrating the environmental performance of chemical processes and products are beginning to emerge. Chemical engineers can and should play a key role in the development of this next generation of design tools, which will help to create more energy-efficient, mass-efficient, and intricately networked industrial processes—an industrial ecology.


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