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CHAPTER 8

EVALUATING ENVIRONMENTAL PERFORMANCE DURING PROCESS SYNTHESIS

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

8.1 INTRODUCTION

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

The art and craft of creating chemical processes is the topic of a number of excellent textbooks (see, for example, Douglas, 1988). A fundamental theme that arises in each of these texts is that the design process proceeds through a series of steps each involving an evaluation of the process performance.

At the earliest stages of a design, only the most basic features of a process are proposed. These include the raw materials and chemical pathway to be used, as well as the overall material balances for the major products, by-products and raw materials. Large numbers of design alternatives are screened at this early design stage, and the screening tools used to evaluate the alternatives must be able to efficiently handle large numbers of alternative design concepts. As design concepts are screened, a select few might merit further study. Preliminary designs for the major pieces of equipment to be used in the process need to be specified for the design options that merit further study. Material flows for both major and minor by-products are estimated. Rough emission estimates, based on analogous processes, might be considered. At this development stage, where fewer design alternatives are considered, more effort can be expended in evaluating each design alternative, and more information is available to perform the evaluation. If a design alternative appears attractive at

this stage, a small scale pilot plant of the process might be constructed and a detailed process flow sheet for a full-scale process might be constructed. Very few new design ideas reach this stage, and the investments made in evaluating design alternatives at this level are substantial. Therefore, process evaluation and screening tools can be quite sophisticated.

Traditionally, evaluations of environmental performance have been restricted to the last stages of this engineering design process, when most of the critical design decisions have already been made. A better approach would be to evaluate environmental performance at each step in the design process. This would require, however, a hierarchy of tools for evaluating environmental performance. Tools that can be efficiently applied to large numbers of alternatives, using limited information, are necessary for evaluating environmental performance at the earliest design stages. More detailed tools could be employed at the development stages, where potential emissions and wastes have been identified. Finally, detailed environmental impact assessments would be performed as a process nears implementation. The goal of this Chapter, and Chapter 11, is to present a hierarchy of tools for evaluating the environmental performance of chemical processes. Three tiers of environmental performance tools will be presented. The first tier of tools, presented in Section 8.2, are appropriate for situations where only chemical structures and the input-output structure of a process is known. Section 8.3 describes a second tier of tools, which are appropriate for evaluating the environmental performance of preliminary process designs. This tier includes tools for estimating wastes and emissions. Finally, Section 8.4 introduces methods for the detailed evaluation of flowsheet alternatives, which will be discussed in Chapter 11.

8.2 TIER 1 ENVIRONMENTAL PERFORMANCE TOOLS

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. Evaluation methods, including environmental performance evaluations, must be rapid, relatively simple, and must rely on the simplest of process material flows. This Section will describe methods for performing environmental evaluations at this level.

As a simple example, consider two alternative processes for the manufacture of methyl methacrylate. Billions of pounds of methyl methacrylate are manufactured annually. Methyl methacrylate can be manufactured through an acetone-cyanohydrin pathway:

$$(CH_3)_2\ C{=}O + HCN \rightarrow HO\text{-}C(CH_3)_2\text{-}CN\ Y\ C_3H_3N + H_2O$$

(Acetone + hydrogen cyanide → acetone cyanohydrin)

$$HO\text{-}C(CH_3)_2\text{-}CN + H_2SO_4 \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}NH_2(H_2SO_4)$$

(acetone cyanohydrin → methacrylamide sulfate)

the methacrylamide sulfate is then cracked forming methacrylic acid and methylmethacrylate

$$CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}NH_2(H_2SO_4) + CH_3OH\ Y\ CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH$$

$$\rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}O\text{-}CH_3$$

Alternatively, methyl methacrylate can be manufactured with isobutylene and oxygen as raw materials.

$$CH_3\text{-}(C{=}CH_2)\text{-}CH_3 + O_2 \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)H + H_2O$$
isobutylene + oxygen → methacrolein

$$CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)H + 0.5\ O_2 \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH$$
methacrolein → methacrylic acid

$$CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH + CH_3OH \rightarrow CH_3\text{-}(C{=}CH_2)\text{-}(C{=}O)\text{-}O\text{-}CH_3 + H_2O$$
methacrylic acid + methanol (in sulfuric acid) → methylmethacrylate

What would be an appropriate method for evaluating these alternatives for synthesizing methyl methacrylate? The first step in answering this question is to select a set of criteria to be used in the evaluation. In traditional methods of process synthesis, cost is the most common screening criterion. To evaluate alternative processes, such as the two processes used in the synthesis of methyl methacrylate, the value of the product could be compared to the cost of the raw materials. Such an evaluation would require data on the raw material input requirements, product and by-product output, and market values of all of the materials. Approximate stoichiometric and cost data for the methyl methacrylate processes (Chang, 1996; Rudd, et al. 1981) are provided in Table 8-1.

Table 8.1 Stoichiometric and cost data for two methyl methacrylate synthesis routes

Compound	*Pounds produced or pounds of raw material required per pound of methyl methacrylate**	*Cost per pound*[1]
Acetone-cyanohydrin route		
Acetone	-.68	$0.43
Hydrogen cyanide	-.32	$0.67
Methanol	-.37	$0.064
Sulfuric acid	-1.63	$0.04
Methyl methacrylate	1.00	$0.78
Isobutylene route		
Isobutylene	-1.12	$0.31
Methanol	-0.38	$0.064
Pentane	-0.03	$0.112
Sulfuric acid	-0.01	$0.04
Methyl methacrylate	1.00	$0.78

* A negative stoichiometric index indicates that a material is consumed; a positive index indicates that it is produced in the reaction;
[1]Data from Chang (1996)

The raw material costs per pound of methyl methacrylate are simply the stoichiometric coefficients,

multiplied by the cost per pound. For the first pathway, the raw material costs per pound of methyl methacrylate are:

0.68 * $0.43 + 0.32 * $0.67 + 0.37 * $0.064 + 1.63 * 0.04 = $0.60 pound of methyl methacrylate

For the isobutylene route, a similar calculation leads to a cost of $0.37 per pound of methyl methacrylate. From this simple evaluation, it is clear that the isobutylene route has lower raw material costs than the acetone-cyanohydrin route, and is probably economically preferable. It is important to note, however, that raw material costs are not the only cost factor. Different reaction pathways may lead to very different processing costs. A reaction run at high temperature or pressure may require more energy or expensive capital equipment than an alternative pathway with more expensive raw materials. Or, raw materials may be available as byproducts from other processes at a lower cost than market rates. So, simple evaluations of raw material costs should only be used in a qualitative fashion. Nevertheless, they provide a simple screening method for chemical pathways and may lead to rapid elimination of alternatives where the raw material inputs are more valuable than the products.

In addition to a simple economic criterion, simple environmental criteria should be available for screening designs, based on input-output data. Selecting a single criterion or a few simple criteria that will characterize a design's potential environmental impacts is not a simple matter. As noted elsewhere in this text, a variety of impact categories could be considered, ranging from the potential of emissions to contribute to global warming, to human health concerns. Not all of these potential impacts can be estimated effectively. Further, if only input-output data are available, there may not be sufficient information to estimate some environmental impacts. For example, estimates of global warming impacts of a design would require data on energy demands, which are often not available at this design stage.

One set of environmental criteria that can be rapidly estimated, even at the input-output level of design, are the persistence, bioaccumulation and toxicities of the input and output materials. Chapter 5 described, in some detail, how these parameters can be estimated based on chemical structure. Consider how this might be applied to the problem of evaluating the methyl methacrylate reaction pathways. Persistence, bioaccumulation, and ecotoxicity for each of the compounds listed in Table 8.1 are listed in Table 8.2.

Table 8.2 Stoichiometric, bioaccumulation and persistence data for two synthesis routes

Compound	*Persistence (atmospheric half life[1])*	*Aquatic half-life (Biodegradation index)*	*Bioaccumulation (Bioconcentration factor)*
Acetone-cyanohydrin process			
Acetone	52 days	weeks	3.2
Hydrogen cyanide	1 year	weeks	3.2
Methanol	17 days	days-weeks	3.2
Sulfuric acid[2]			
Methyl methacrylate	7 hours	weeks	2.3
Isobutylene process			
Isobutylene	2.5 hours	weeks	12.6
Methanol	17 days	days-weeks	3.2
Pentane	2.6 days	days-weeks	81
Sulfuric acid[2]			
Methyl methacrylate	7 hours	weeks	2.3

[1] the atmospheric half life is based on the reaction with the hydroxyl radical and assumes an ambient hydroxyl radical concentration of $1.5*10^6$ molecules per cubic centimeter and 12 hours of sunlight per day

[2] The group contribution method does not estimate an atmospheric reaction rate for sulfuric acid , however, it=s lifetime in the atmosphere is short due to reactions with ammonia

The values for persistence and bioaccumulation reported in Table 8-2 were calculated using the ECOWIN software package, which is based on the methods described in Chapter 5. In Chapter 5, classification schemes, based on the values of persistence and bioaccumulation factors, were presented. These classifications are partially reproduced in Table 8-3.

Table 8.3 Classification schemes for persistence and bioaccumulation

Biodegradation		
Rapid	>60% degradation over 1 week	Rating index = 0
Moderate	>30% degradation over 28 days	Rating index = 1
Slow	<30% degradation over 28 days	Rating index = 2
Very Slow	<30% degradation over more than 28 days	Rating index = 3

Bioaccumulation		
High Potential	8.0> Log K_{oc}>4.3 or BCF>1000	Rating index = 3
Moderate Potential	4.3> Log K_{ow}>3.5 or 1000>BCF>250	Rating index = 2
Low Potential	3.5> Log K_{oc} or 250>BCF	Rating index = 1

Comparing these classifications to the values presented in Table 8.2 leads to the conclusion that none

of the reactants or products in either scheme bioaccumulate or are persistent in the environment. This is a qualitative assessment. Later in this Section, quantitative evaluations will be discussed, and for the purposes of those quantitative assessments the numerical ratings, given in Table 8.3 are useful. In this case all of the compounds would have biodegradation ratings of 1 and bioaccumulation ratings of 1.

While persistence and bioaccumulation can generally be evaluated using the structure-activity methods described in Chapter 5, toxicity is more problematic. Some structure-activity relationships exist for relating chemical structures to specific human health or ecosystem health endpoints, but often the correlations are limited to specific classes of compounds. The ideal toxicity parameter would recognize a variety of potential human and ecosystem health endpoints and would be readily accessible. No such parameter exists. A variety of simple toxicity surrogates have been employed, however, including Threshold Limit Values, Permissible Exposure Levels, inhalation reference concentrations, and oral response factors. Each of these are described below.

Threshold Limit Values (TLVs) and Permissible Exposure Levels (PELs) are parameters that were developed to address the problem of establishing workplace limits for concentrations of chemicals. TLVs and PELs are the maximum concentrations of chemicals workers can be safely exposed to in occupational settings. TLVs and PELs reflect the different health impacts of chemicals and variations in exposure pathways. TLV and PEL are defined as follows:

> *Threshold Limit Value (TLV)* The TLV is the airborne concentration to which an individual can be exposed in a workplace environment. The concentration is set at a level for which no adverse effects would be expected over a worker=s lifetime. A number of threshold limit values can be cited for a chemical, depending on the length of the exposure. In this chapter, the TLVs will be time-weighted averages for an 8 hour workday and a 40 hour work week. The concentration, again, is the level to which nearly all workers can be exposed without adverse effects. TLVs are established by the American Conference of Governmental Industrial Hygienists (ACGIH) (www.acgih.org).
>
> *Permissible Exposure Levels (PELs)* The United States Occupational Safety and Health Administration (OSHA) has the authority to place limits on exposures to chemicals in the workplace. The workplace limits set by OSHA are referred to as PELs and the PELs set by OSHA are generally similar to the TLVs set by the ACGIH.

A set of representative TLV and PEL values are given in Table 8.4.

Table 8.4 Threshold Limit Values and Permissible Exposure Levels for Selected Compounds (adapted from Crowl and Louvar, 1990; note that these values are periodically updated. Readers interested in current values of these parameters should consult the appropriate web site)

Compound	*TLV (ppm)*	*PEL (ppm)*
Acetaldehyde	100	100
Acetic acid	10	10
Acetone	750	750
Acrolein	0.1	0.1
Ammonia	25	25
Arsine	0.05	0.05
Benzene	10	10
Biphenyl	0.2	0.2
Bromine	0.1	0.1
Butane	800	-
Carbon Monoxide	50	35
Chlorine	0.5	0.5
Chloroform	10	2
Cyclohexane	300	300
Cyclohexene	300	300
Cyclopentane	600	-
1,1 Dichloroethane	200	100
1,2 Dichloroethylene	200	200
Diethyl ketone	200	-
Dimethylamine	10	10
Ethylbenzene	100	100
Ethyl chloride	1000	1000
Ethylene dichloride	1	1
Ethylene oxide	1	1
Formaldehyde	1	1
Gasoline	300	-
Heptane	400	400
Hexachloroethane	1	1
Isobutyl alcohol	50	50
Isopropyl alcohol	400	400
Maleic anhydride	0.25	0.25
Methyl ethyl ketone	200	200
Naphthalene	10	10
Nitric acid	2	2
Nitric oxide	25	25
Nitrogen dioxide	3	3
Phosgene	0.1	0.1
Sulfur dioxide	2	2
Trichloroethylene	50	50
Vinyl chloride	5	5

The values in Table 8.4 have a number of features that are worth comment. First note that the TLV

and PEL values are generally quite similar. In addition, note that for some compounds, TLV data are available, but PEL values are not. This is because TLV values represent a scientific and professional assessment of hazards, while PEL values have legal implications in defining workplace conditions. Thus, it is not unusual for a TLV value to be established before a PEL value. Because of the greater number of chemicals for which there are reported values, there is a tendency to use TLV data in screening methodologies rather than PEL values.

One method of using TLV and PEL values to define a toxicity index is to use the inverse of the TLV (or PEL) (see, for example, Horvath, et al., 1995).

$$\text{Environmental Index} = 1/(\text{TLV or PEL}) \qquad \text{(Equation 8.1)}$$

The concept is simple. Higher TLVs imply that higher exposures can be tolerated with no observable health effect B implying a lower health impact. A simple way to express this relationship mathematically is with an inverse relationship, as shown in Equation 8.1.

Using the TLV (or PEL) as a surrogate for all toxicity impacts is a gross simplification. The TLV only accounts for direct human health effects, and even for this purpose, it is dangerous to use the TLV as a measure of relative health impact. Figure 8.1 illustrates one of the pitfalls of using TLV as an indicator of relative human health impact.

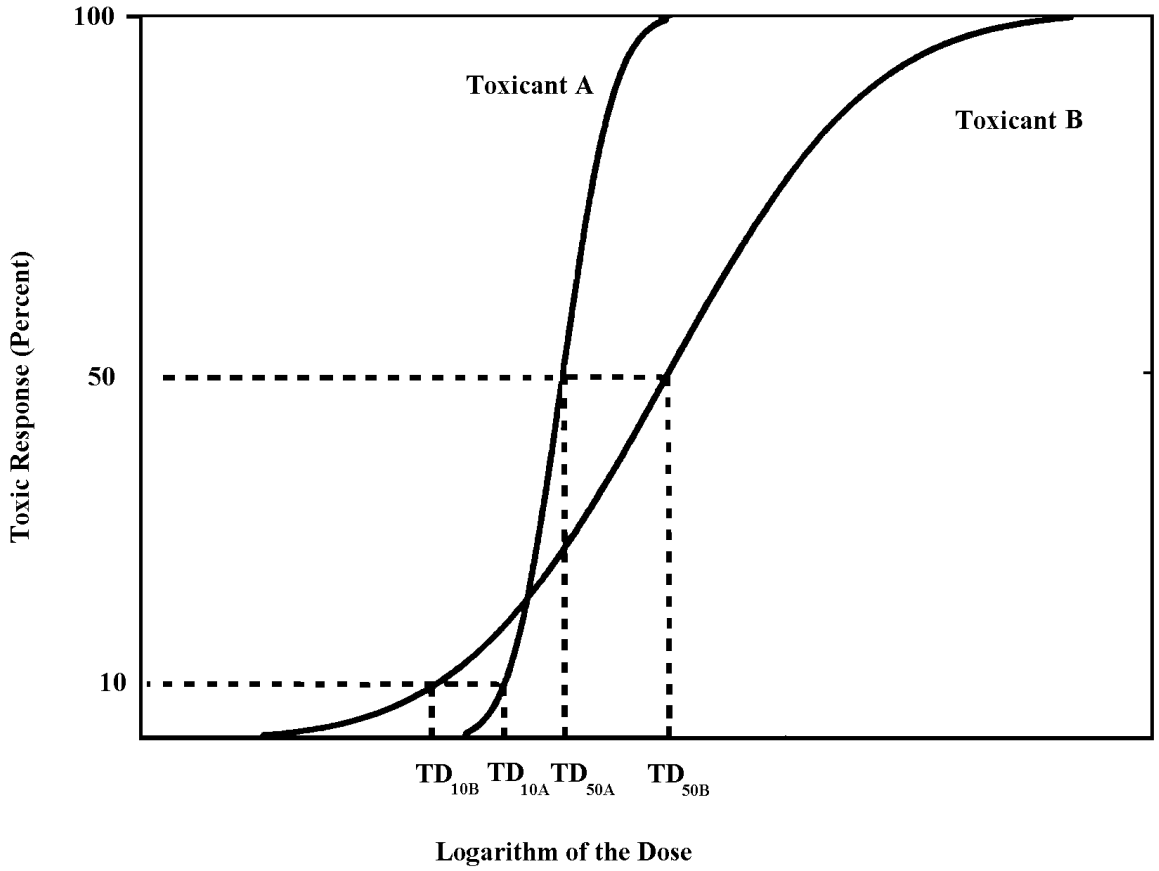

Figure 8.1 Dose response curves for two compounds that have different relative Threshold Limit Values, depending on how the effect level is defined (Crowl and Louvar, 1990)

Figure 8.1 shows the toxic response of two chemicals, A and B, as a function of dose. Chemical A has a higher threshold concentration, at which no toxic effects are observed, than chemical B. Once the threshold dose is exceeded, however, chemical A has a greater response to increasing dose than chemical B. If the TLV were based on the dose at which 10% of the population experienced health effects, then chemical B would have a lower TLV than chemical A. In contrast, if the TLV were based on the dose at which 50% of the population experienced a health impact, chemical A would have the lower TLV. So, which chemical is more toxic? The answer depends on the precise definition of toxicity and the specifics of the dose response relationship.

This conceptual example is designed to illustrate the dangers of using simple indices as precise, quantitative indicators of environmental impacts. There is value, however, in using these simple indicators in rough, qualitative evaluations of potential environmental impacts.

An additional limitation of TLV values is that they do not consider ingestion pathways. An alternative measure of potential toxicities might incorporate both inhalation and ingestion exposure pathways. Such a system has been developed by the U.S. EPA using data available from the EPA's IRIS (Integrated Risk Information System) database. IRIS compiles a wide range of available data on individual compounds (www.epa.gov/ngispgm3/iris/subst/index.html). Three data elements that are of use in assessing potential toxicities are the inhalation reference concentration, the oral ingestion slope factor, and the unit risk. As defined in the IRIS documentation, a reference concentration is "an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious noncancer effects during a lifetime". The inhalation reference concentration is in some ways related to the TLV, and ratios of the TLVs of different compounds would be expected to be similar to the ratios of the inhalation reference concentrations.

A oral slope factor characterizes response to ingestion of a compound and is defined as "the slope of a dose response curve in the low dose region. When low dose linearity cannot be assumed, the slope factor is the slope of the straight line from 0 dose (and 0 excess risk) to the dose at 1% excess risk. An upper bound on this slope is usually used instead of the slope itself. The units for the slope factor are usually expressed as $(mg/kg\text{-}day)^{-1}$." (U.S. EPA, IRIS, 1999)

The unit risk is "the upper bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 microgram/L in water and 1 microgram/cubic meter in air".

A simple example may clarify the meaning of these indicators of toxicity. Consider the data available on IRIS (August, 1999) for acrylonitrile. IRIS lists acrylonitrile as a probable human carcinogen. Non-carcinogenic effects include inflammation of nasal tissues. The reference concentration for inhalation is given as 0.002 mg/m^3. Lifetime exposure to this concentration is likely to be without an appreciable risk of nasal tissue inflammation and degeneration. The oral slope factor for carcinogenic risk is given as 0.54 $(mg/kg\text{-}day)^{-1}$**.** A 100 kg person exposed to 54 mg per day would have a 1% excess risk. The potential individual excess lifetime cancer risk (i.e., unit risk) is $6.8*10^{-5}$ per $microgram/m^3$. For a region with a population of 100,000, this corresponds to approximately 6.8 potential excess cancer cases per year based on a lifetime exposure of 1 $microgram/m^3$of acrylonitrile (i.e., an upper bound of the lifetime risk is 6.8 in 100,000). Note that 6.8 represents an upper bound and the actual risk may be much less.

The U.S. EPA has used data such as reference concentrations, oral slope factors, and unit risk factors to determine toxicity weighting for approximately 600 compounds reported through

the Toxic Release Inventory. A complete description of the methodology and the toxicity weights are available at www.epa.gov/opptintr/env_ind/index.html. To briefly summarize, the EPA assembled up to four preliminary human health toxicity weights for each compound: cancer-oral, cancer-inhalation, non-cancer-oral and non-cancer-inhalation. For each exposure pathway (oral and inhalation) the greater of the cancer and non-cancer toxicity weights was chosen. If data on only one exposure pathway were available, then the toxicity weight for that pathway was assigned to both pathways, however, if there is evidence that no exposure occurs through one of the pathways, then the toxicity weight for that pathway was assigned a value of 0.

The toxicity weights were based on the values for unit risks and slope factors. A sample of the scheme used to assign toxicity weights is given in Table 8.5.

Table 8.5. Assignment of Toxicity weights for Chemicals with Cancer Health Effects

Range of oral slope factor (SF) (risk per mg/kg-day	*Range of inhalation unit risk factor (UR) (risk per mg/m^3)*	*Known or probable carcinogen*	*Possible carcinogen*
SF<0.005	UR<0.0014	10	1
0.005<SF<0.05	0.0014<UR<0.014	100	10
0.05<SF<0.5	0.014<UR<0.14	1000	100
0.5<SF<5	0.14<UR<1.4	10,000	1000
5<SF<50	1.4<UR<14	100,000	10,000
50>SF	UR>14	1,000,000	100,000

For the acrylonitrile, a probable carcinogen with an oral slope factor of 0.54, the oral toxicity weight would be 10,000. The toxicity weight for inhalation, based on a unit risk of $6.8*10^{-5}$ per (microgram/m^3) or .068 per (milligram/m^3), would be 1000. The overall toxicity weight would be based on the larger of the two values. Table 8.6 provides a sampling of toxicity weights. The compounds listed are the same compounds for which TLV data were listed in Table 8-3. The data are somewhat more sparse than the TLV data.

Table 8.6 Selected Toxicity Weights drawn from the U.S. EPA's Environmental Indicators project

Compound	*Overall inhalation toxicity factor*	*Overall oral toxicity factor*
Acetaldehyde	*1000*	*1000*
Acetic acid		
Acetone		
Acrolein	*100000*	*100000*
Ammonia	*100*	*100*
Arsine		
Benzene	*100*	*100*
Biphenyl	*100*	*100*
Bromine		
Butane		
Carbon Monoxide		
Chlorine	*10*	*10*
Chloroform	*1000*	*100*
Cyclohexane		
Cyclohexene		
Cyclopentane		
1,1 Dichloroethane	*1000*	*1000*
1,2 Dichloroethylene	*100*	*100*
Diethyl ketone		
Dimethylamine		
Ethylbenzene		
Ethyl chloride		
Ethylene dichloride		
Ethylene oxide	*10000*	*10000*
Formaldehyde	*100*	*10*
Gasoline		
Heptane		
Hexachloroethane	*10*	*1000*
Isobutyl alcohol		
Isopropyl alcohol		
Maleic anhydride	*10*	*10*
Methyl ethyl ketone	*10*	*1*
Naphthalene		
Nitric acid		
Nitric oxide		
Nitrogen dioxide		
Phosgene		
Sulfur dioxide		
Trichloroethylene		
Vinyl chloride	*10000*	*10000*

As a case study of the use of TLVs and toxicity weights in evaluating toxicity, consider once again the two routes for producing methyl methacrylate. Stoichiometric, TLV, reference concentration, and slope factor data for the two pathways are shown in Table 8.7

Table 8.7 Stoichiometric, TLV, reference concentration and slope factor data for two methyl methacrylate synthesis routes

Compound	*Pounds produced or pounds of raw material required per pound of Methyl methacrylate**	*1/TLV (ppm)*	*Overall inhalation toxicity factor*	*Overall oral toxicity factor*
Acetone-cyanohydrin process				
Acetone	*-.68*	*1/750*	*NA*	*NA*
Hydrogen cyanide	*-.32*	*1/10*	*1000*	*100*
Methanol	*-.37*	*1/200*	*10*	*10*
Sulfuric acid	*-1.63*	*1/2(est.)*	*10,000*	*1*
Methyl methacrylate	*1.00*	*1/100 (PEL)*	*10*	*10*
Isobutylene process				
Isobutylene	*-1.12*	*1/200 (est)*	*NA*	*NA*
Methanol	*-0.38*	*1/200*	*10*	*10*
Pentane	*-0.03*	*1/600*	*NA*	*NA*
Sulfuric acid	*-0.01*	*1/2 (est)*	*10,000*	*1*

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

Both the TLVs and toxicity weights in Table 8-4 indicate that the major health concerns associated with the two reaction pathways are due to sulfuric acid, and to a lesser extent, hydrogen cyanide.

Once these data, together with data on persistence and bioaccumulation, are known for the reactants and products, some composite index for the overall input-output structure could be established. Ideally, the index would be based on the emission rates, weighted by measures of persistence, bioaccumulation and toxicity. In preliminary screenings, however, it is highly unlikely that detailed information will be available on emission rates. Therefore, approximations for emission rates are required. One possible approach is to use flow rate, based on stoichiometry, as a surrogate for emissions. This surrogate for emissions can then be weighted by an appropriate index.

In choosing weighting factors and an overall index for assessing environmental performance at this early stage of a design, it is important to recognize that there is no single correct choice. Many different indices have been employed. This chapter will illustrate two types of approaches that have appeared frequently in the literature. One approach is to use toxicity

as a weighting factor. In this approach, the overall environmental index for a reaction is typically calculated as:

$$\text{Environmental index} = \text{Ó}\ |\nu_i| * (TLV_i)^{-1} \qquad \text{(Equation 8-2)}$$

Where $|\nu_i|$ is the absolute value of the stoichiometric coefficient of reactant or product i, TLV_i is the threshold limit value of reactant or product i, and the summation is taken over all reactants and products. For the acetone-cyanohydrin process:

$$\text{Index} = 0.68*(1/750) + 0.32*(1/10) + 0.37*(1/200) + 1.63*(1/2) + 1*(1/100) = 0.86$$

For the acetone-cyanohydrin process, the index calculated using Equation 8-2 is 0.86, and for the isobutylene process, the index is 0.01, indicating a preference for the isobutylene process. This is because the indices are dominated by the contribution of sulfuric acid, which is used at a lower rate in the isobutylene process.

Alternatively, the toxicity factors developed by the U.S. EPA could be used, rather than the TLVs. In this case:

$$\text{Environmental index} = \text{Ó}\ |\nu_i| * (\text{maximum of oral and inhalation weighting factor}) \qquad \text{(Equation 8-3)}$$

Using this approach, the index for the acetone-cyanohydrin process would be:

$$\text{Index} = 0.68 * (0) + 0.32 * (1000) + 0.37 * (10) + 1.63 * (10{,}000) + 1 * (10) = 16{,}600$$

For the isobutylene process, the index is 100, again indicating a preference for the isobutylene process.

Another approach, that appears in preliminary environmental assessments, employs persistence, bioaccumulation and toxicity factors. Combining these factors into a composite environmental index requires that the factors be placed in a common unit system. This is generally done by assigning ratings to the persistence, bioaccumulation, and toxicity parameters. Table 8.2 gave rating factors for persistence and bioaccumulation for the two methyl methacrylate pathways. Ratings for human toxicity are more difficult to assign. In the evaluation of chemicals under the Toxic Substances Control Act, the U.S. EPA employs three levels of concern for human toxicity (Wagner, et al., 1995)

High concern:

Evidence of adverse effects in human populations

Conclusive evidence of severe effects in animal studies

Moderate concern
- Suggestive animal studies
- Data from close chemical analogue
- Compound class known to produce toxicity

Low concern
- Chemicals that do not meet the criteria for moderate or high concern

Based on these criteria, the human toxicity concerns of the two methyl methacrylate pathways would be dominated by the concerns associated with sulfuric acid. Thus, the two pathways would have very similar levels of toxicity concern unless the relative amounts of sulfuric acid used were incorporated into the evaluation. As noted earlier, the bioaccumulation and persistence of the compounds associated with the two pathways were also identical, therefore the overall environmental performance of the two pathways could be viewed as virtually identical.

Table 8.8 Evaluation of acrylonitrile pathways based on persistence, bioaccumulation and toxicity

Pathway	***Persistence of raw materials and products***	***Bioaccumulation potential of raw materials and products***	***Toxicity of raw materials and products***
Ammoxidation of propylene	*All raw materials and products on a time scale of weeks; rating index =1*	*Bioaccumulation potential of all raw materials and products is low**; rating index = 1***	*Toxicity is dominated by sulfuric acid, **which is a respiratory toxicant and a suspected carcinogen; rating index = 2***
Cyanation of ethylene oxide	*All raw materials and products on a time scale of weeks; rating index =1*	*Bioaccumulation potential of all raw materials and products is low**; rating index = 1***	*Toxicity is dominated by sulfuric acid**, which is a respiratory toxicant and a suspected carcinogen; rating index = 2***

Table 8.8 provides a set of three ratings for each pathway. These three ratings could be combined into a single index, or they could be retained in the matrix format shown in the Table.

To summarize, the environmental performance of the two pathways for manufacturing methyl methacrylate were evaluated based on economics, toxicity and a combined assessment of persistence, bioaccumulation and toxicity. All of the approaches indicate a preference for the isobutylene pathway. A similar case study with a different result is given in Example 8.1.

Example 8.1 *Acrylonitrile can be produced via the ammoxidation of propylene or via the cyanation of ethylene oxide. Stoichiometric, TLV, persistence, bioaccumulation, toxicity and cost data for the two reactions are given below.*

a.) Estimate the persistence and bioaccumulation potential of the two pathways

b.) Evaluate the toxicity potential of the two pathways

c.) Suggest which pathway is preferable based on environmental and economic criteria

ammoxidation of propylene:

$$C_3H_6 + NH_3 + 1.5\ O_2 \rightarrow C_3H_3N + 3\ H_2O$$

cyanation of ethylene oxide

$$C_2H_4 + 0.5\ O_2 \rightarrow C_2H_4O$$
$$C_2H_4O + HCN\ Y\ HOC_2H_4CN \rightarrow C_3H_3N + H_2O$$

Stoichiometric, TLV and cost data for two acrylonitrile synthesis routes

Compound	*Stoichiometry**	*1/TLV (ppm)* $^{-1}$	*Cost per pound*
Ammoxidation of propylene			
Proplyene	-1.1	1/10,000	$0.13
Ammonia	-0.4	1/25	$0.07
Acrylonitrile	1	1/2	$0.53
Hydrogen cyanide	0.1	1/10	$0.68
Acetonitrile	0.03	1/40	$0.65
Cyanation of ethylene oxide			
Ethylene	-0.84	1/10,000	$0.23
Hydrogen cyanide	-0.6	1/10	$0.68
Acrylonitrile	1	1/2	$0.53
Carbon dioxide	0.3	1/5,000	

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

[1]*Data from Chang (1996)*

Solution

a.) Estimate the persistence and bioaccumulation potential of the two pathways

Based on the data in the Table below, the materials used in the two pathways have comparable, relatively low persistence and bioaccumulation potentials.

Stoichiometric, bioaccumulation and persistence data for two acrylonitrile synthesis routes

Compound	*Persistence (atmospheric half life[1])*	*Aquatic half-life (Biodegradation index)*	*Bioaccumulation*
Ammoxidation of propylene			
Proplyene	4.9 hours	weeks	4.6
Ammonia	NA[2]	weeks	3.2
Acrylonitrile	30.5 hours	weeks	3.2
Hydrogen cyanide	1 year	weeks	3.2
Acetonitrile	1 year	weeks	3.2
Cyanation of ethylene oxide			
Ethylene	15 hours	weeks	1.1
Hydrogen cyanide	1 year	weeks	3.2
Acrylonitrile	30.5 hours	weeks	3.2
Carbon dioxide	-	-	-

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

[1] the atmospheric half life is based on the reaction with the hydroxyl radical and assumes an ambient hydroxyl radical concentration of $1.5*10^6$ molecules per cubic centimeter and 12 hours of sunlight per day

[2] The group contribution method does not estimate an atmospheric reaction rate for ammonia, however, it's lifetime in the atmosphere is short due to reactions with acid gases

The values for persistence and bioaccumulation were calculated using the ECOWIN software package, which is based on the methods described in Chapter 5.

b.) Evaluate the toxicity potential of the two pathways

As shown in the Table and calculations below, the toxicity is dominated by the product, acrylonitrile, so the two pathways have very similar environmental performance indices

Stoichiometric, TLV, reference concentration and slope factor data for two acrylonitrile synthesis routes

Compound	*Pounds produced or pounds of raw material required per pound of acrylonitrile**	*TLV (ppm)*	*Overall inhalation toxicity factor*	*Overall oral toxicity factor*
Ammoxidation of propylene				
Proplyene	*-1.1*	*>10,000*	*1*	*1*
Ammonia	*-0.4*	*25*	*100*	*100*
Acrylonitrile	*1*	*2*	*1000*	*10,000*
Hydrogen cyanide	*0.1*	*10*	*1000*	*100*
Acetonitrile	*0.03*	*40*	*100*	*100*
Cyanation of ethylene oxide				
Ethylene	*-0.84*	*>10,000*	*1*	*1*
Hydrogen cyanide	*-0.6*	*10*	*1000*	*100*

Acrylonitrile	*1*	*2*	*1000*	*10,000*
Carbon dioxide	*0.3*	*5000*		

** A negative index indicates that a material is consumed; a positive index indicates that it is produced*

For the acetone B cyanohydrin process, the environmental index based on the TLV and the index based on EPA=s toxicity weights are is given by:

TLV Index = 1.1/10,000 + 0.4/25 + 1/2 + 0.1/10 + 0.03/40 =0.53
EPA Index = 1.1 * 1 + 0.4 * 100 + 1. * 10,000 + 0.1 * 1,000 + 0.03 * 100 = 10,144

For the cyanation of ethylene oxide the indices are :
TLV Index =0.84/10,000 + 0.6/10 + 1/2 + 0.3/5000 = 0.56
EPA Index = 0.84 * 1 + 0.6 * 1000 + 1. * 10,000 = 10,600

Based on these criteria, the human toxicity concerns of the two acrylonitrile pathways would be dominated by the concerns associated with acrylonitrile. Thus, the two pathways would have very similar levels of toxicity concern. As noted earlier, the bioaccumulation and persistence of the compounds associated with the two pathways were also identical, therefore the overall environmental performance of the two pathways could be viewed as virtually identical.

Evaluation of acrylonitrile pathways based on persistence, bioaccumulation and toxicity

Pathway	**Persistence of raw materials and products**	**Bioaccumulation potential of raw materials and products**	**Toxicity of raw materials and products**
Ammoxidation of propylene	All raw materials and products on a time scale of weeks; rating index =1	Bioaccumulation potential of all raw materials and products is low; rating index = 1	Toxicity is dominated by the product, acrylonitrile, which is a probable carcinogen; high concern rating
Cyanation of ethylene oxide	All raw materials and products on a time scale of weeks; rating index =1	Bioaccumulation potential of all raw materials and products is low; rating index=1	Toxicity is dominated by the product, acrylonitrile, which is a probable carcinogen; high concern rating

c.) Suggest which pathway is preferable based on environmental and economic criteria
A simple economic evaluation considers the raw material costs. For the ammoxidation of propylene, the economic index is given by:

Index = 1.1 * ($0.13) + 0.4 * ($0.07) = $0.17
Alternatively, an index could include raw material costs minus the value of salable by-products:
Index = 1.1 * ($0.13) + 0.4 * ($0.07) - 0.1 * ($0.68) - 0.03 * ($0.65) = $0.14

For the cyanation of ethylene oxide, the economic index is:

Index = $0.84 * $0.23 + 0.6 * $0.68 = $0.60

Thus, the ammoxidation of propylene is preferable to the cyanation of ethylene oxide on a cost basis; the pathways have comparable environmental characteristics.

Section 8.2 Questions for Discussion

1. What criteria would you suggest for evaluating the environmental performance of reaction pathways?
2. Can you suggest alternatives to stoichiometric coefficients for weighting environmental indices in evaluating reaction pathways?
3. What are the strengths and limitations of the environmental performance criteria described in this section?

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