Chapter 8

Evaluating Environmental Performance During Process Synthesis

Evaluating Environmental Performance During Process Synthesis

By the end of this section you should:

- Be able to assess the environmental impacts of chemical processes at the input-output level
- Be able to assess the environmental impacts of chemical processes at the level of a process block diagram
- Be able to estimate emissions from chemical processes based on a block diagram

Contents

Evaluating Environmental Performance During Process Synthesis

- 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.

- Here we deal with 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

Evaluating Environmental Performance During Process Synthesis

The search for "greener chemistry" 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.

Evaluating Environmental Performance During Process Synthesis

- The design process proceeds through a series of steps each involving an evaluation of the associated environmental impacts.

- At the earliest stages of a design, only the most basic features of a process are proposed. These include the raw materials and chemical pathway to be used, as well as the overall material balances for the major products, by-products and raw materials.

- Large numbers of design alternatives are screened at this early design stage, and the screening tools used to evaluate the alternatives must be able to handle efficiently large numbers of alternative design concepts.

Evaluating Environmental Performance During Process Synthesis

- 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.

Evaluating Environmental Performance During Process Synthesis

- 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.

8.1 Introduction

A hierarchy of tools for evaluating the environmental performance of chemical processes. (3단계 평가)

- **1st Tier**： *useful when only chemical structures and input-output structure of a process is known*
- **2nd Tier**: *useful when evaluating environmental performance of preliminary process designs*
- **3rd Tier**： *method for the detailed evaluation of flowsheet alternatives*

8.2 Tier 1 Environmental Performance Tools

- At the early stage of design, only the most elementary data on *raw materials, products, and byproducts,* of the chemical process may be available and large number of design alternatives may need to be considered.

- Evaluation methods, including environmental performance evaluation, must be rapid, relatively simple and must rely on the simplest of process materials flows.

8.2.1 Economic Criteria

- Traditional Manufacturing Route of MMA.

$$(CH_3)_2C{=}O + HCN \rightarrow HO{-}(CH_3)_2{-}CN$$

(acetone + hydrogen cyanide → acetone cyanohydrin)

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

(acetone cyanodydrin → methacrylamide sulfate)

Methacrylamide sulfate is then cracked, forming methacrylic acid and MMA

$$CH_3{-}(C{=}CH_2){-}(C{=}O){-}NH_2(H_2SO_4) + CH_3OH$$

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

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

8.2.1 Economic Criteria

- Alternative route (isobutylene + O_2 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 → methacrylein)

$$CH_3\text{–}(C{=}CH_2)\text{–}(C{=}O)H + 0.5\ O_2 \rightarrow CH_3\text{–}(C{=}CH_2)\text{-}(C{=}O)\text{-}OH$$

(methacrylein → 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)

Methyl methacrylate

From Wikipedia, the free encyclopedia

Methyl methacrylate is an organic compound with the formula $CH_2{=}C(CH_3)CO_2CH_3$. This colourless liquid, the methyl ester of methacrylic acid (MAA) is a monomer produced on a large scale for the production of polymethyl methacrylate (PMMA).

Production

[edit]

The compound is manufactured by several methods, the principal one being the acetone cyanohydrin (ACH) route, using acetone and hydrogen cyanide as raw materials. The intermediate cyanohydrin is converted with sulfuric acid to a sulfate ester of the methacrylamide, methanolysis of which gives ammonium bisulfate and MMA. Although widely used, the ACH route coproduces substantial amounts of ammonium sulfate. Some producers start with an isobutylene or, equivalently, *tert*-butanol, which is sequentially oxidized first to methacrolein and then to methacrylic acid, which is then esterified with methanol. Propene can be carbonylated in the presence of acids to isobutyric acid, which undergoes subsequent dehydrogenation.[1] The combined technologies afford more than 3 billion kilograms per year. MMA can also be prepared from methyl propionate and formaldehyde.[2]

Uses

[edit]

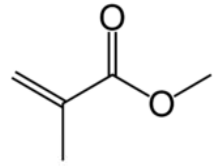
Main article: Acrylate polymers

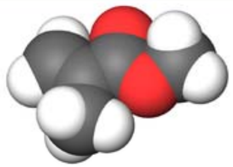
The principal application, consuming approximately 80% of the MMA, is the manufacture of polymethyl methacrylate acrylic plastics (PMMA). Methyl methacrylate is also used for the production of the co-polymer methyl methacrylate-butadiene-styrene (MBS), used as a modifier for PVC.

Structure	
Dipole moment	1.6-1.97 D
Hazards	
MSDS	Methyl methacrylate MSDS
Main hazards	flammable
Flash point	2 °C (autoignition 435 °C)

Properties	
Molecular formula	$C_5H_8O_2$
Molar mass	100.12 g/mol
Appearance	colourless liquid
Density	0.94 g/cm³
Melting point	-48 °C (225 K)
Boiling point	101 °C (374 K)
Solubility in water	1.5 g/100 ml (25 °C)
Viscosity	0.6 cP at 20 °C

Methyl methacrylate





Methyl methacrylate	
IUPAC name	[show]
Other names	MMA, 2-(methoxycarbonyl)-1-propene

Methacrylic acid

From Wikipedia, the free encyclopedia

Methacrylic acid, abbreviated MAA, is an organic compound. This colourless, viscous liquid is a carboxylic acid with an acrid unpleasant odor. It is soluble in warm water and miscible with most organic solvents. Methacrylic acid is produced industrially on a large scale as a precursor to its esters, especially methyl methacrylate (MMA). The methacrylates have numerous uses, most notably in the manufacture of polymers with trade names such as Lucite and Plexiglas. MAA occurs naturally in small amounts in the oil of Roman chamomile.

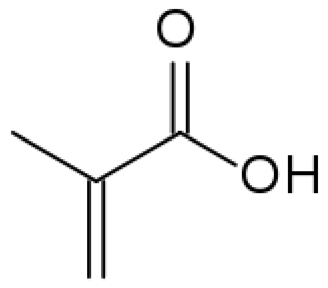
Production and properties

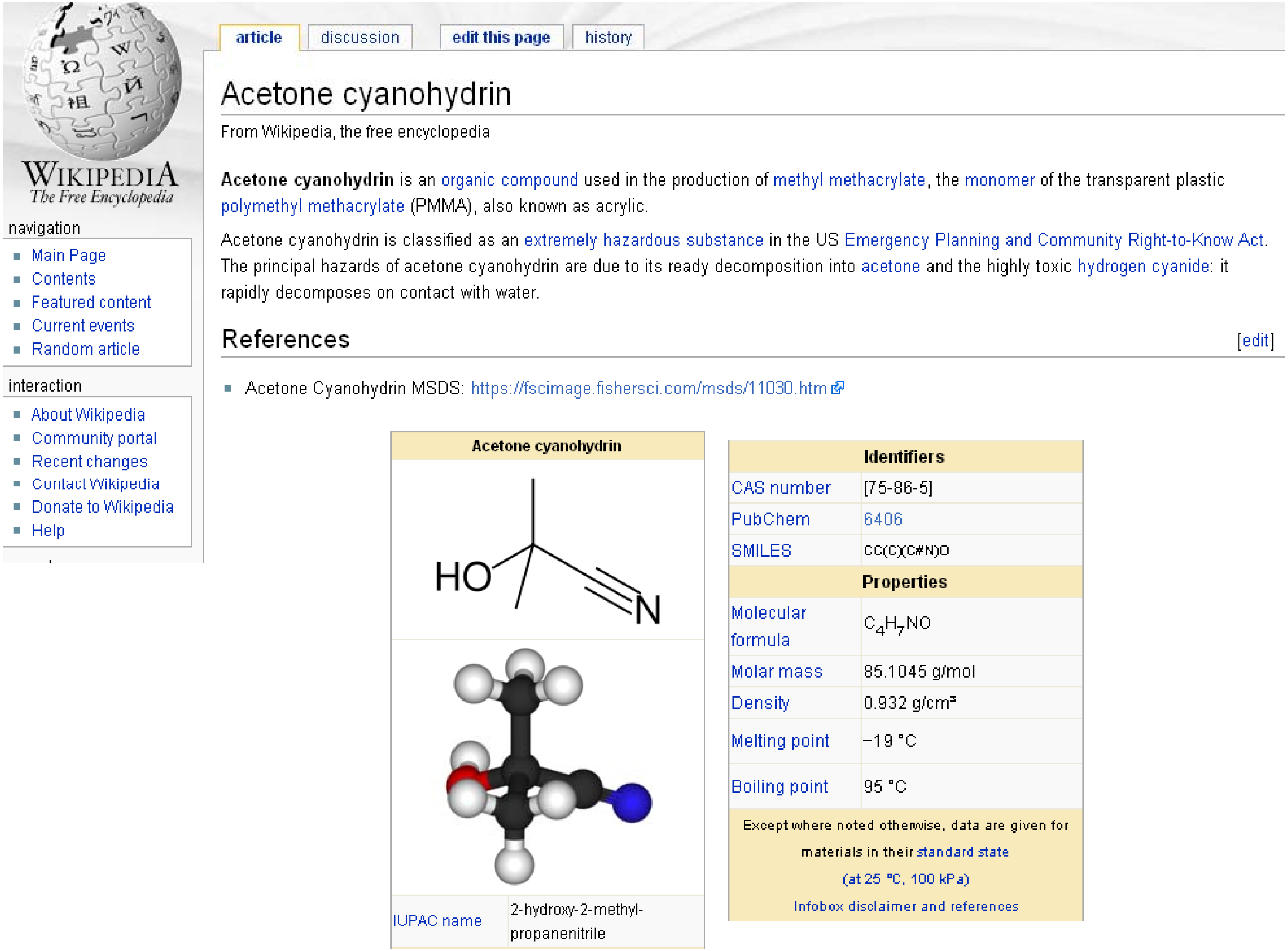
[edit]

More than 3 billion kilograms of methyl methacrylate (MMA) are produced annually, and a significant fraction of the manufacturing processes proceed via the intermediacy of MAA (the dominant process, the "ACH route," does not). Isobutylene and *tert*-butanol, are oxidized sequentially to methacrolein and then to MAA, which is then largely esterified.[1]

Methacrylic acid was first obtained in the form of its ethyl ester by treating phosphorus pentachloride with oxyisobutyric ester.[2] It is, however, more readily obtained by boiling citra- or meso-brompyrotartaric acids with alkalis. It crystallizes in prisms. When fused with an alkali, it forms propionic acid. Sodium amalgam reduces it to isobutyric acid. A polymeric form of methacrylic acid was described in 1880.[3]

	Properties
Molecular formula	$C_4H_6O_2$
Molar mass	86.06 g/mol
Density	1.015 g/cm^3
Melting point	14 - 15 °C
Boiling point	161 °C

Methacrylic acid	
	
IUPAC name	[show]
Other names	MAA, 2-methyl-2-propenoic acid
Identifiers	
CAS number	[79-41-4]



Acetone cyanohydrin

From Wikipedia, the free encyclopedia

Acetone cyanohydrin is an organic compound used in the production of methyl methacrylate, the monomer of the transparent plastic polymethyl methacrylate (PMMA), also known as acrylic.

Acetone cyanohydrin is classified as an extremely hazardous substance in the US Emergency Planning and Community Right-to-Know Act. The principal hazards of acetone cyanohydrin are due to its ready decomposition into acetone and the highly toxic hydrogen cyanide: it rapidly decomposes on contact with water.

References

[edit]

- Acetone Cyanohydrin MSDS: https://fscimage.fishersci.com/msds/11030.htm

Acetone cyanohydrin

IUPAC name	2-hydroxy-2-methyl-propanenitrile

Identifiers	
CAS number	[75-86-5]
PubChem	6406
SMILES	CC(C)(C#N)O
Properties	
Molecular formula	C_4H_7NO
Molar mass	85.1045 g/mol
Density	0.932 g/cm³
Melting point	−19 °C
Boiling point	95 °C

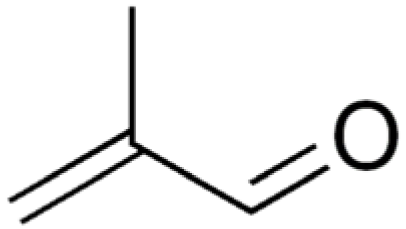
Except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)

Infobox disclaimer and references

Methacrolein

From Wikipedia, the free encyclopedia

Methacrolein, or methacrylaldehyde, is an unsaturated aldehyde. It is a clear, colorless, flammable liquid. Industrially, the primary use of methacrolein is in the manufacture of polymers and synthetic resins. Exposure to methacrolein is highly irritating to the eyes, nose, throat and lungs.

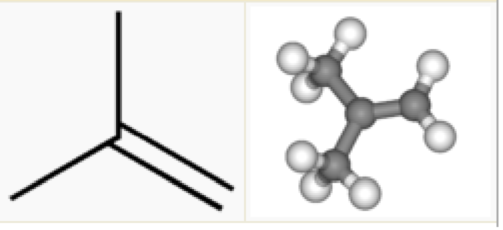
Methacrolein	
	
IUPAC name	[show]
Other names	Methacrolein Methacrylaldehyde Isobutenal
Identifiers	
CAS number	[78-85-3]
SMILES	[show]
Properties	
Molecular formula	C_4H_6O
Molar mass	70.09 g/mol
Density	0.8470 g/cm^3
Melting point	-81 °C
Boiling point	69 °C

Isobutylene

From Wikipedia, the free encyclopedia

Isobutylene (or 2-methylpropene) is a hydrocarbon of significant industrial importance. It is a four-carbon branched alkene (olefin), one of the four isomers of butylene. At standard temperature and pressure it is a colorless flammable gas.

Isobutylene[1][2]



Properties	
Molecular formula	C_4H_8
Molar mass	56.11 g mol^{-1}
Appearance	Colorless gas
Density	0.5879 g/cm^3
Boiling point	-6.9 °C, 266 K, 20 °F
Solubility in water	Insoluble

Uses

Isobutylene is used as an intermediate in the production of a variety of products. It is reacted with methanol and ethanol in the manufacture of the gasoline oxygenates methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE), respectively. Alkylation with butane produces isooctane, another fuel additive. Isobutylene is also used in the production of methacrolein. Polymerization of isobutylene produces butyl rubber (polyisobutylene). Antioxidants such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) are produced by Friedel-Crafts alkylation of phenols using isobutylene.

Manufacture [edit]

Isobutylene can be isolated from refinery streams by reaction with sulfuric acid, but the most common industrial method for its production is by catalytic dehydrogenation of isobutane.[3] In the 1990s, the production of isobutylene increased dramatically as the demand for oxygenates such as MTBE grew. Key manufacturers of this product are Texas Petrochemicals and Lyondell in North America.

Safety [edit]

Isobutylene is a highly flammable gas and presents an explosion danger. Usually stored as a compressed gas, if released it may produce an oxygen-deficient atmosphere that presents an asphyxiation hazard.[2]

What is an appropriate method for evaluating alternative for synthesizing MMA ?

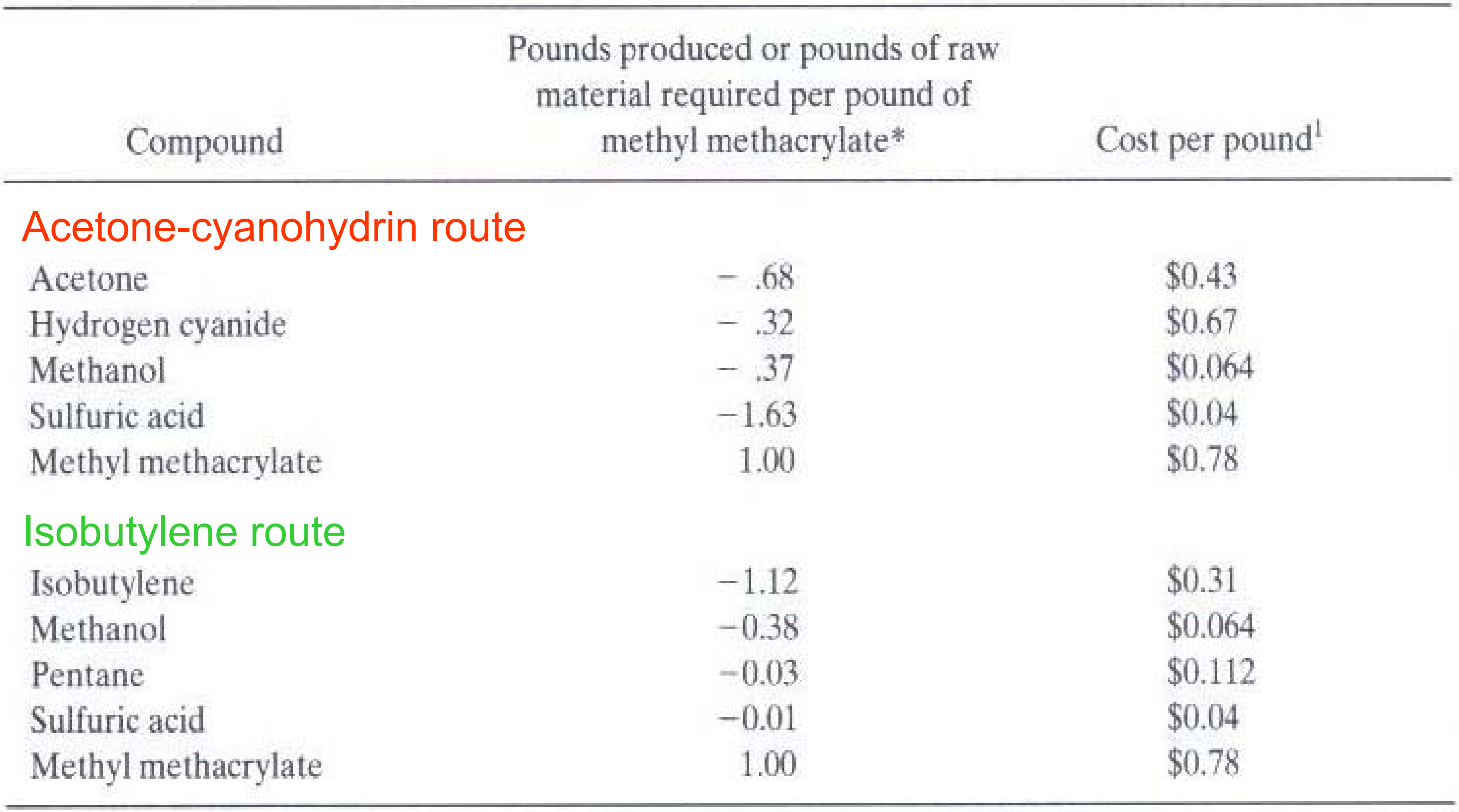
- The first step in answering this question is to select a set of criteria to be used in evaluation.

- In traditional process, cost is most common screening criterion. In alternative routes, value of the product could be compared to the cost of the raw materials. Such an evaluation would require data on raw material input requirements, product and byproduct output, market values of all of the materials.

- Approximate stoichiometry and cost data for MMA processes are provided in Table 8.2-1

Table 8.2-1

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

The raw material costs per pound of MMA

Acetone-cyanohydrin route

0.68 x \$0.43 + 0.32 x \$0.67 + 0.37 x \$0.064 + 1.64 x \$0.04 = \$0.60

Isobutylene route

1.12 x \$0.31 + 0.38 x \$0.064 + 0.03 x \$0.112 + 0.01 x \$0.04 = \$0.37

Isobutylene route is probably economically preferable. However raw material costs are not 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 raw materials. Or, raw materials may be available as byproducts from other processes at lower cost than market rates.

8.2.2 Environmental Criteria

- In addition to a simple economic criterion, simple *environmental criteria* should be available for screening designs, based on input-output data. Selecting a single criteria or a few simple criteria that will characterize a design’s potential environmental impact is not a simple matter.

- A variety of impact categories could be considered, ranging from 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 demand, which are often not available at this design stage.

8.2.2 Environmental Criteria

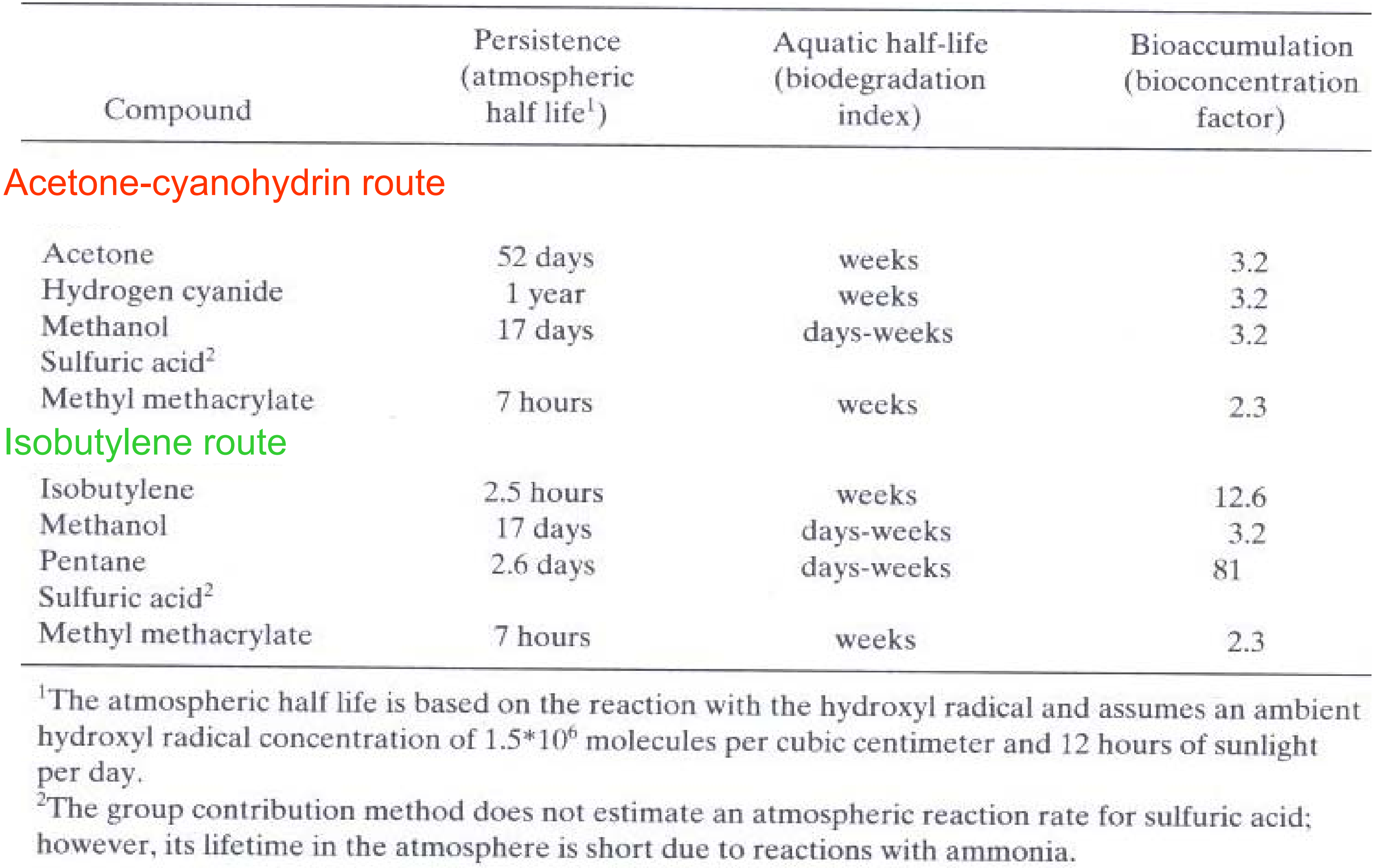
One set of environmental criteria that can be *rapidly* estimated, even at the input-output level of design, are

- **persistence**
- **bioaccumulation**
- **toxicity**

of input-output materials. Chapter 5 described how these parameters can be estimated based on chemical structure.

Consider how this might be applied to the problem of evaluating the MMA production pathways. Persistence and bioaccumulation for each of the compounds listed in Table 8.2.1 are listed in Table 8.2-2.

Table 8.2-2
Bioaccumulation and persistence data for two synthesis routes



Compound	Persistence (atmospheric half life[1])	Aquatic half-life (biodegradation index)	Bioaccumulation (bioconcentration factor)
Acetone-cyanohydrin route			
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 route			
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

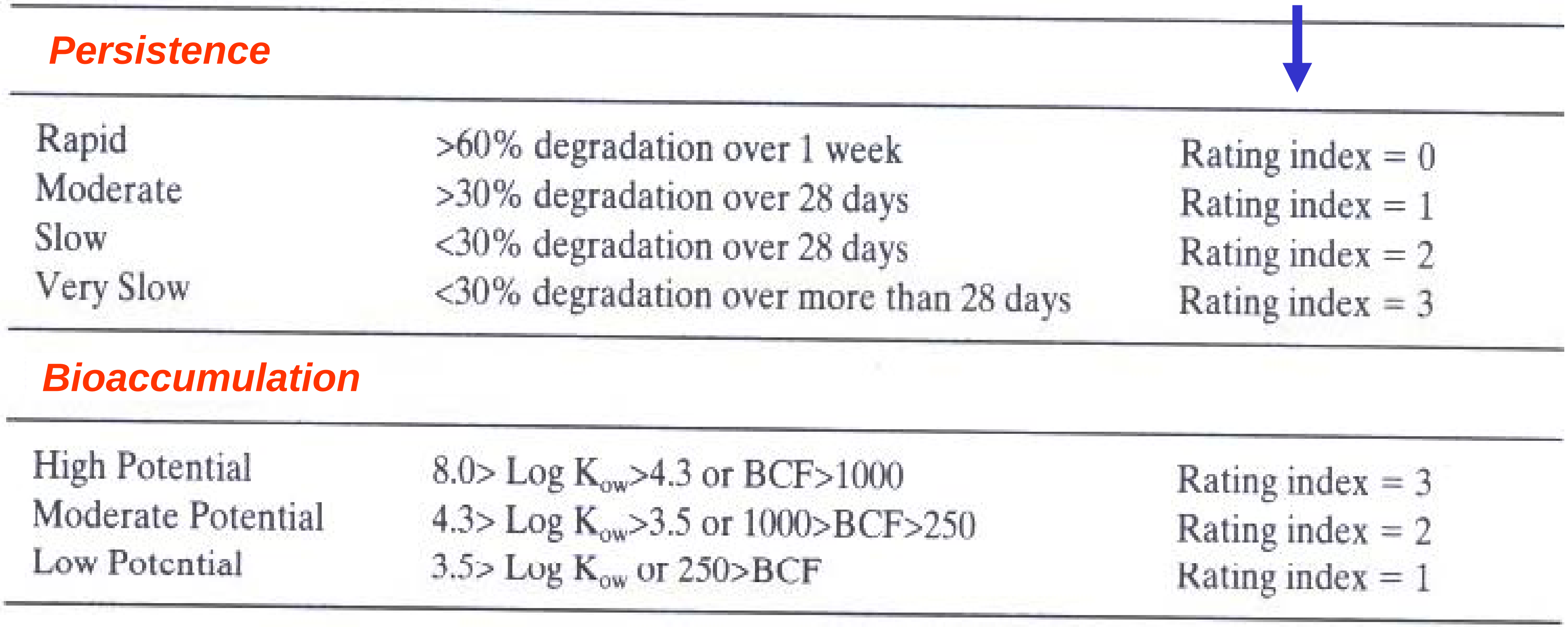
[1] The atmospheric half life is based on the reaction with the hydroxyl radical and assumes an ambient hydroxyl radical concentration of $1.5*10^6$ molecules per cubic centimeter and 12 hours of sunlight per day.

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

Table 8.2-3

Classification schemes for persistence and bioaccumulation

Numerical ratings for quantitative assessment



Persistence		
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_{ow}>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_{ow} or 250>BCF	Rating index = 1

All the compounds would have persistence ratings of 1 and bioaccumulation ratings of 1

8.2.3 TLVs, PELs, and RELs

While persistence and bioaccumulation can generally be evaluated using the structure-activity methods, 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. A variety of simple **toxicity surrogates**

- **TLV** *(Threshold Limit Values)*
- **PEL** *(Permissible Exposure Limits)*
- **REL** *(Recommended Exposure Limits)*
- Inhalation Reference Concentrations
- Oral Response Factors

These parameters are to address the problem of establishing workplace limits for concentrations of chemicals.

Threshold Limit Values (TLVs)

- One type of airborne concentration limit for individual exposures in the workplace environment

- Concentration is set at a level for which no adverse effects would be expected over a worker's lifetime *(TLV is a time-weighted averages for 8-hr workday and a 40-hr workweek)*

- The concentration is the level to which nearly all workers can be exposed without adverse effect

- They are established by the *American Conference of Governmental Industrial Hygienists* (ACGIH) *http://www.acgih.org*

Permissible Exposure Limits (PELs)

- The United States Occupational Safety and Health Administration (OSHA: 노동안전위생국) has the legal authority to place limits on exposures to chemicals in the workplace.

- The workplace limits set by OSHA are referred to as PELs, and are set by OSHA in a manner similar to the setting of TLVs by ACGIH

Recommended Exposure Limits (RELs)

- The National Institute for Occupational Safety and Health (NIOSH: 국립직업안전건강연구소), under the Center for Disease Control and Prevention (CDC: 질병관리센터), publishes RELs based on toxicity research.

- As the research complement to OSHA, NIOSH set RELs that are intended to assist OSHA in the setting and revising of the legally binding PELs.

- Because no rule-making process is required for NIOSH to set RELs, these values are frequently more current than the OSHA PELs.

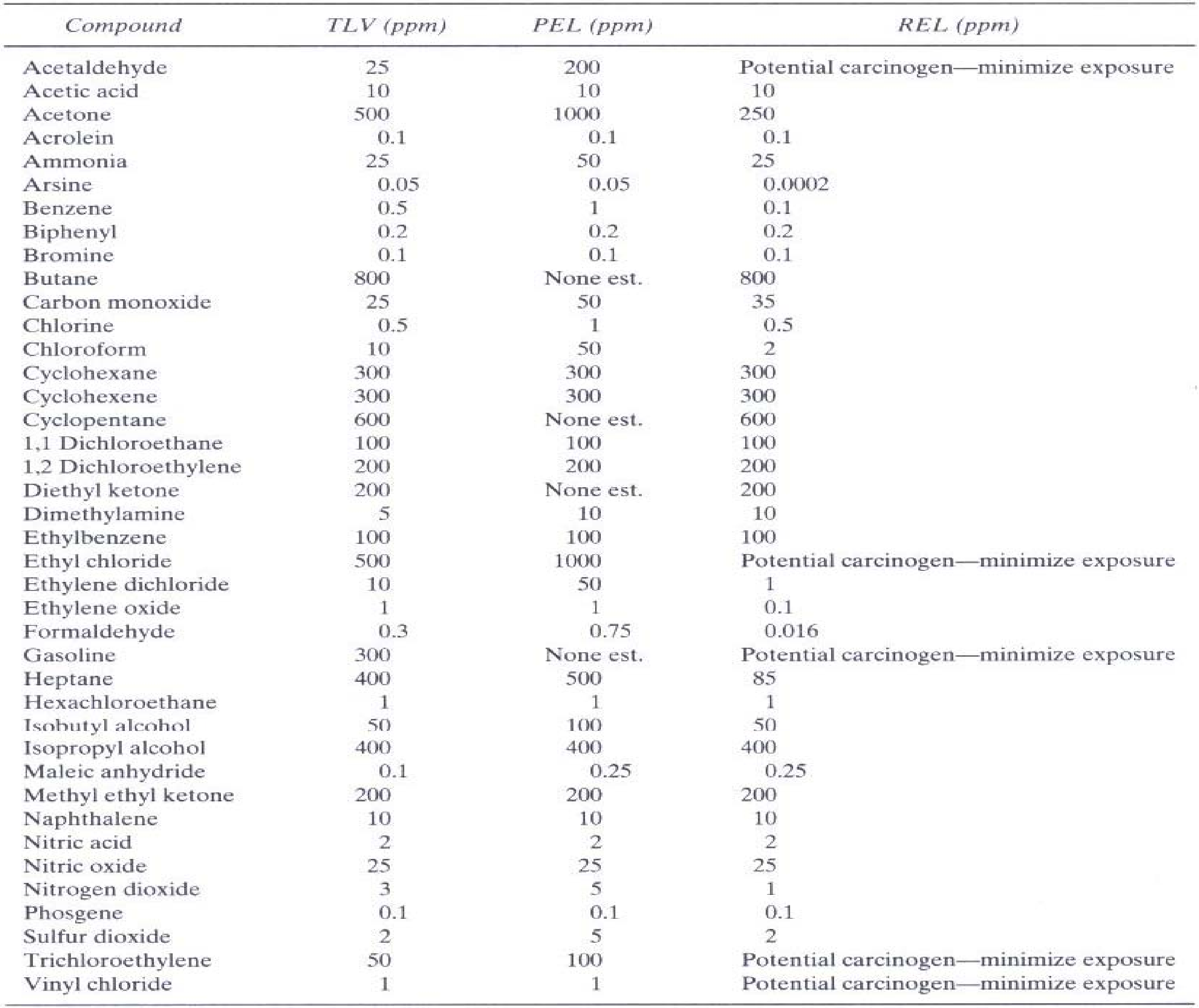
The values of TLV, PEL, and REL

TLV, PEL and REL values in Table 8.2-4 are generally quite similar, but some of differences are worthy of comment.

- TLV values represent a scientific and professional assessment of hazards
- PEL values have legal implications in defining workplace conditions. It directly influenced by political, economic and feasibility issues.
- NIOSH, as the research complement to OSHA, is not affected by these external issues and can set their limits in a purely research environment.
- Because RELs do not face the same practicality issues as the PELs, NIOSH has chosen not to set safe levels of exposures to these substances.
- It is not unusual for TLV or REL 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 TLA or REL data in screening methodologies rather than PEL values.

Table 8.2-4

TLVs, PELs and RELs for selected compounds.
Note that these values continue to be periodically updated.



Compound	*TLV (ppm)*	*PEL (ppm)*	*REL (ppm)*
Acetaldehyde	25	200	Potential carcinogen—minimize exposure
Acetic acid	10	10	10
Acetone	500	1000	250
Acrolein	0.1	0.1	0.1
Ammonia	25	50	25
Arsine	0.05	0.05	0.0002
Benzene	0.5	1	0.1
Biphenyl	0.2	0.2	0.2
Bromine	0.1	0.1	0.1
Butane	800	None est.	800
Carbon monoxide	25	50	35
Chlorine	0.5	1	0.5
Chloroform	10	50	2
Cyclohexane	300	300	300
Cyclohexene	300	300	300
Cyclopentane	600	None est.	600
1,1 Dichloroethane	100	100	100
1,2 Dichloroethylene	200	200	200
Diethyl ketone	200	None est.	200
Dimethylamine	5	10	10
Ethylbenzene	100	100	100
Ethyl chloride	500	1000	Potential carcinogen—minimize exposure
Ethylene dichloride	10	50	1
Ethylene oxide	1	1	0.1
Formaldehyde	0.3	0.75	0.016
Gasoline	300	None est.	Potential carcinogen—minimize exposure
Heptane	400	500	85
Hexachloroethane	1	1	1
Isobutyl alcohol	50	100	50
Isopropyl alcohol	400	400	400
Maleic anhydride	0.1	0.25	0.25
Methyl ethyl ketone	200	200	200
Naphthalene	10	10	10
Nitric acid	2	2	2
Nitric oxide	25	25	25
Nitrogen dioxide	3	5	1
Phosgene	0.1	0.1	0.1
Sulfur dioxide	2	5	2
Trichloroethylene	50	100	Potential carcinogen—minimize exposure
Vinyl chloride	1	1	Potential carcinogen—minimize exposure

Toxicity index

One method of using TLV and PEL values to define a toxicity index is

$$\boxed{\textbf{Environmental Index} = \frac{1}{\textbf{TLV}}}$$

- ***Higher TLV imply higher exposures can be tolerated with no observable health effect, implying a lower health impact.***
- Using TLV as a surrogate for all toxicity impacts is a gross simplification. *TLV only accounts for direct human health effects via inhalation.* It is dangerous to use the TLV as a measure of relative health impact (Fig. 8.2-1).

Which is more toxic?

(depends on definition and dose-response relation)

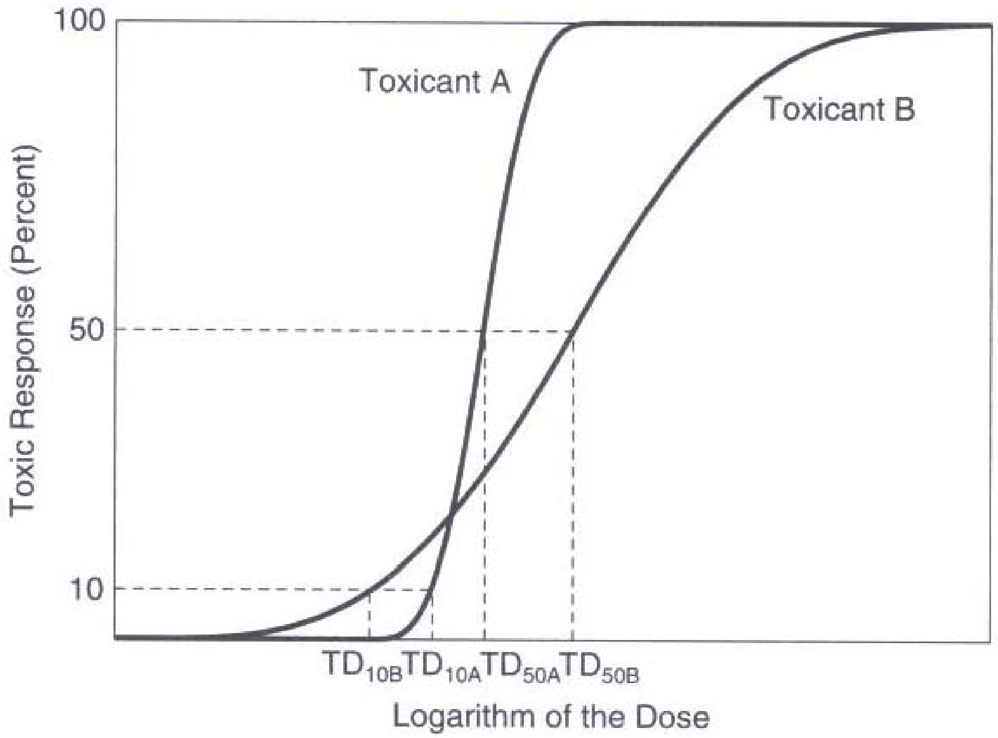


Fig. 8.2-1
Dose response curves for two compounds that have different relative threshold limit value (TLVs), depending on how the effect level is defined (Crowl and Louvar, 1990)

On Fig. 8.2-1

- Chemical A has higher threshold concentration, at which no toxic effects are observed, than B

- Once threshold dose is exceeded, A has greater response to increasing dose than B

- If TLV were based on the dose at which 10 % of the population experienced health effect, then, B would have a lower TLV than A

- If TLV were on dose at which 50 %, A would have lower TLV.

Toxicity Weighting

In 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 US EPA using data available from the EPA's IRIS (Integrated Risk Information System) database.

IRIS complies a wide range of available data on individual compounds (http://www.epa.gov/ngispgm3/iris/subst/index.html)

Three Data Elements useful in **assessing potential toxicities**

- Inhalation Reference Concentration
- the Oral Ingestion Slope Factor
- the Unit Risk

Toxicity Weighting

Three Data Elements useful in ***assessing potential toxicities***

- **Inhalation Reference Concentration**

  ~*some ways related to TLV, and ratios of TLVs of different compounds would be similar to the ratios of the inhalation reference concentration*

- **the Oral Ingestion Slope Factor**

  "*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 to the dose at 1% excess risk. [mg/kg-day]*$^{-1}$"

- **the Unit Risk**

  "*upper bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 μg/L in water and 1 μg/m*^{3} *in air*"

acrylonitrile

IRIS lists acrylonitrile as a **probable human carcinogen**

- **Reference concentration for inhalation** : **0.002 mg/m^3**

  (Lifetime exposure to this concentration is likely to be without an appreciable risk of tissue inflammation and degeneration)

  염증 변질

- **Oral slope factor for carcinogenic risk : 0.54 (mg/kg-day)$^{-1}$**

  (A 100kg person exposed to 100 mg per day would have 0.54 % excess risk)

- **Potential individual excess lifetime cancer risk (i.e., unit risk) : 6.8x10^{-5} per μg/m^3**

  (for region with 100,000 population, about 6.8 potential excess cancer cases based on lifetime exposure of 1 μg/m^3 of acrylonitrile. Note that 6.8 represents an upper bound and the actual risk may be much less.)

Toxic Weights

The US EPA has used data such as reference concentration, oral slope factors, and unit risk factors to determine toxicity weight for approximately 600 compounds reported through the Toxic Release Inventory.

A complete description of the methodology and toxicity weights are available at http://www.epa.gov/opptitr/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.

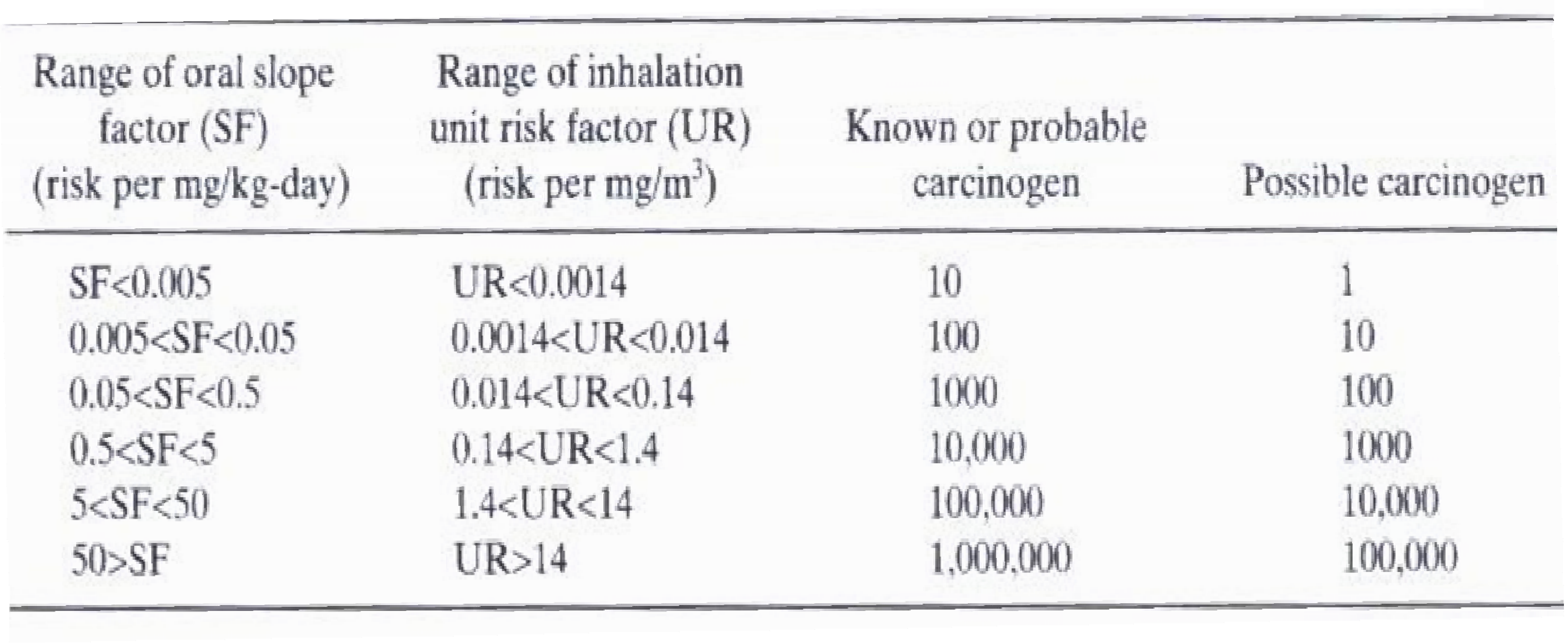
For each exposure pathway (oral and inhalation) the greater of the cancer and non-cancer toxicity weights was chosen. If data on only one exposure pathway were available, then the toxicity weight for that pathway was assigned to both pathways, however, if there is evidence that no exposure occurs through one of the pathway, then the toxicity for that pathway was assigned a value of 0.

Toxic Weights

The toxicity weights were based on the values for unit risks and slope factors. A simple of the scheme used to assigned to toxicity weights is given in Table 8.2-5.

Table 8.2-5

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

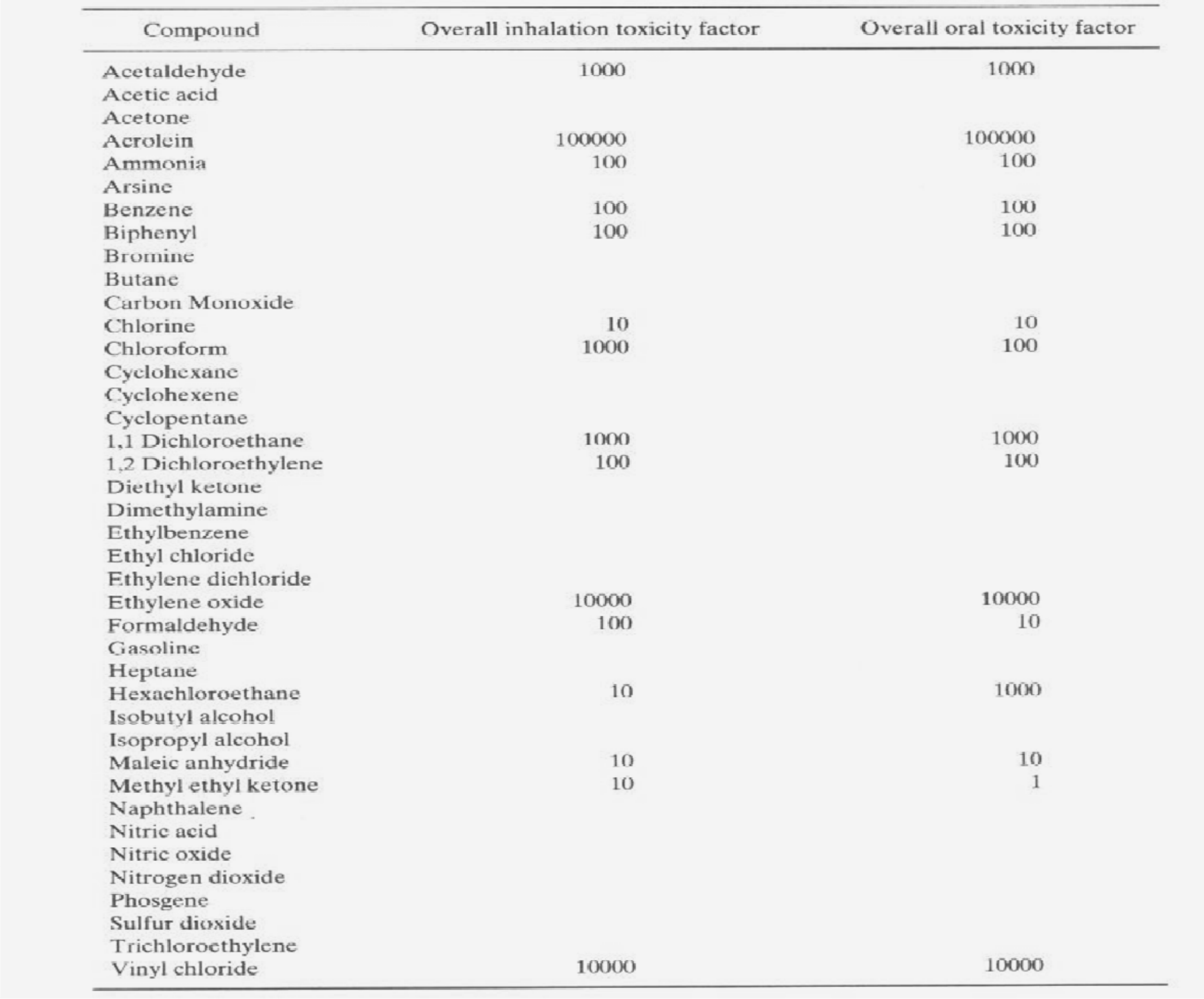
Toxicity weight for acrylonitrile

(EPA project results)

- **Probable carcinogen** with an ***oral*** slope factor of 0.54, the oral toxicity weight would be **10,000**
- Toxicity weight for ***inhalation***, based on a unit risk of $6.8\text{x}10^{-5}$ per (μg/m^3) or 0.068 per (mg/m^3) would be **1,000**
- The overall toxicity weight would be based on the larger of the two values *(**Table 8.2-6** provides a sampling of toxicity weights)*
- the compounds listed are the same compounds for which TLV data were listed in *Table 8.2-3*
- Data are somewhat more sparse than the TLV data

Sparse: 빈약한

Table 8.2-6 Selected toxicity weights drawn from the US 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

8.2.5 Evaluating Alternative Synthesis Pathways

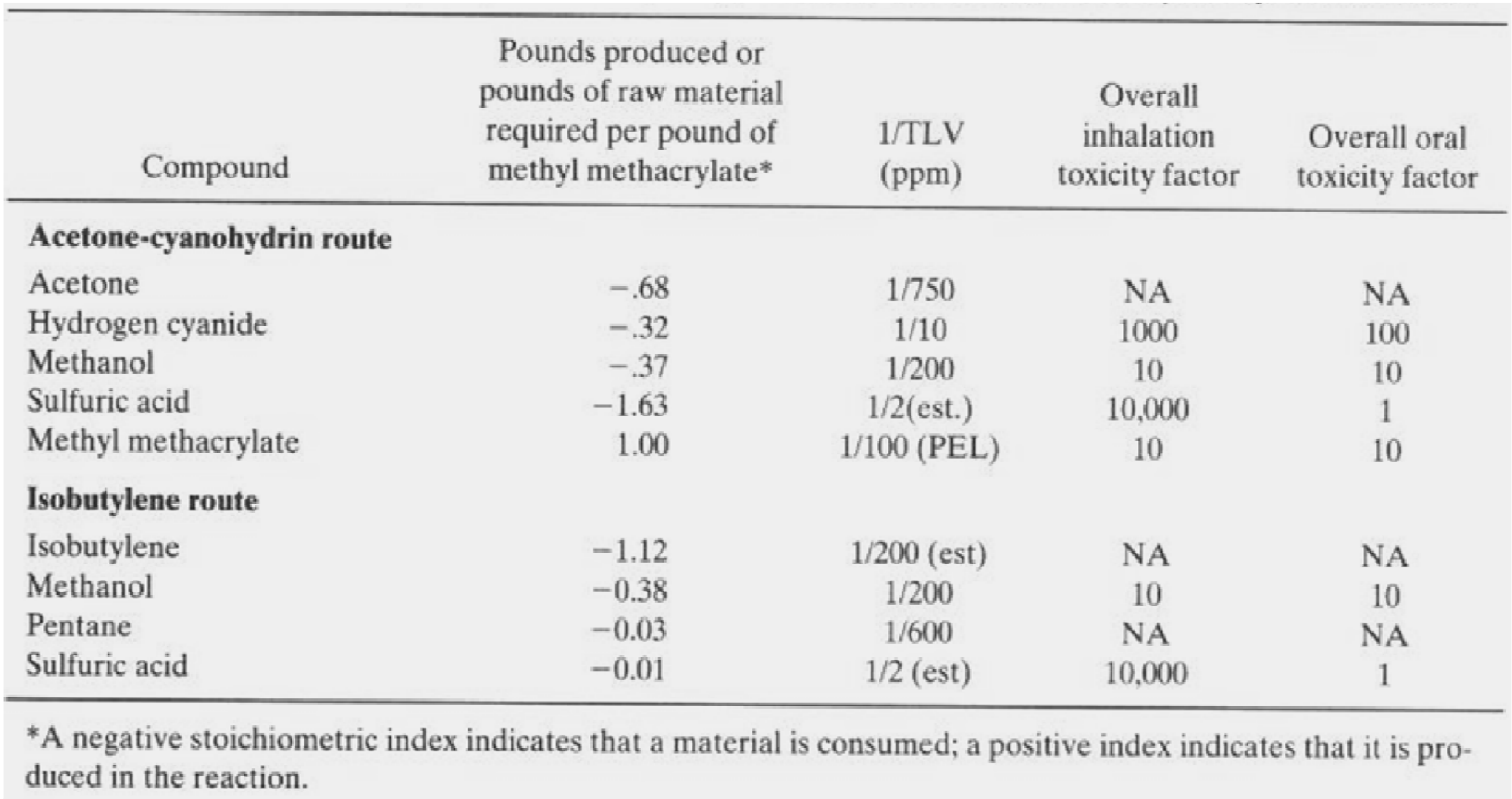
Consider the two routes for producing MMA. Stoichiometric, TLV, and toxicity weight data are in **Table 8.2-7**

- In **Table 8.2-7**, both TLVs and toxicity weights indicate that the major health concerns with the reaction pathways are due to sulfuric acid and to a less extend hydrogen cyanide.

- Once these data and persistence and bioaccumulation are known for reactants and products, some composite index for the overall input-output structure could be established. Ideally the index be based on emission rates, weighted by measure of persistence, bioaccumulation and toxicity.

- No detail emission rates in preliminary screenings ➔ use flow rate based on stoichiometry as a surrogate for emissions.

Table 8.2-7
Stoichiometirc, TLV, and toxicity weight 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 route				
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 route				
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.

8.2.5 Evaluating Alternative Synthesis Pathways

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. (①TLV, ②maximum oral and inhalation weight factor……)

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

$$\textbf{Environmental Index} = \sum |\nu_i| \times (TLV_i)^{-1}$$

where $|\nu_i|$ is the absolute value of the stoichiometric (by mass) coefficient of reactants or product *i* , TLV_i is the threshold limit value (ppm) of reactant or product *i*, and summation is taken over all reactants and products.

8.2.5 Evaluating Alternative Synthesis Pathways

For the acetone-cyanohydrin route:

Environ. Index = 0.68 x (1/750) + 0.32 x (1/10) + 0.37 x (1/200) + 1.63 x (1/2) + 1 x (1/100) = **0.8598**

For the isobutylene process:

Environ. Index = 1.12 x (1/200) + 0.38 x (1/200) + 0.03 x (1/600) + 0.01 x (1/2) = **0.0126**

Isobutylene process is environmentally friendly process due to mainly lower rate of sulfuric acid in isobutylene process.

8.2.5 Evaluating Alternative Synthesis Pathways

Alternatively, the toxicity factors developed by the US EPA could be used, rather than the TLVs.

Environmental Index
$= \sum |\nu_i| \times$ (maximum of oral and inhalation weighting factor)

For acetone-cyanohydrin process:

$$\text{Index} = \overset{\text{acetone}}{0.68 \text{ x } (0)} + \overset{\text{HCN}}{0.32 \text{ x } (1000)} + \overset{CH_3OH}{0.37 \text{ x } (10)}$$
$$+ \underset{H_2SO_4}{1.63 \text{ x } (10{,}000)} + \underset{\text{MMA}}{1 \text{ } (10)} = \mathbf{16{,}633.7}$$

For isobutylene process:

$$\text{Index} = \overset{\text{isobutylene}}{1.12 \text{ x } (0)} + \overset{CH_3OH}{0.38 \text{ x } (10)} + \overset{\text{Pentane}}{0.03 \text{ x } (0)} + \overset{H_2SO_4}{0.01 \text{ x } (10{,}000)}$$
$$= \mathbf{113.8}$$

again indicating a preference for the isobutylene process

8.2.5 Evaluating Alternative Synthesis Pathways

- 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 8.2-2 gave rating factors for persistence and bioaccumulation for the two MMA pathways. Ratings for human toxicity are more difficult to assign.

- In the evaluation of chemicals under the toxic Substances Control Act, the US EPA employs three levels of concern for human toxicity (Wagner, 1995)

8.2.5 Evaluating Alternative Synthesis Pathways

Ratings for human toxicity

In evaluation of chemicals under the Toxic Substances Control Act, EPA employs 3 levels of concern

- **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

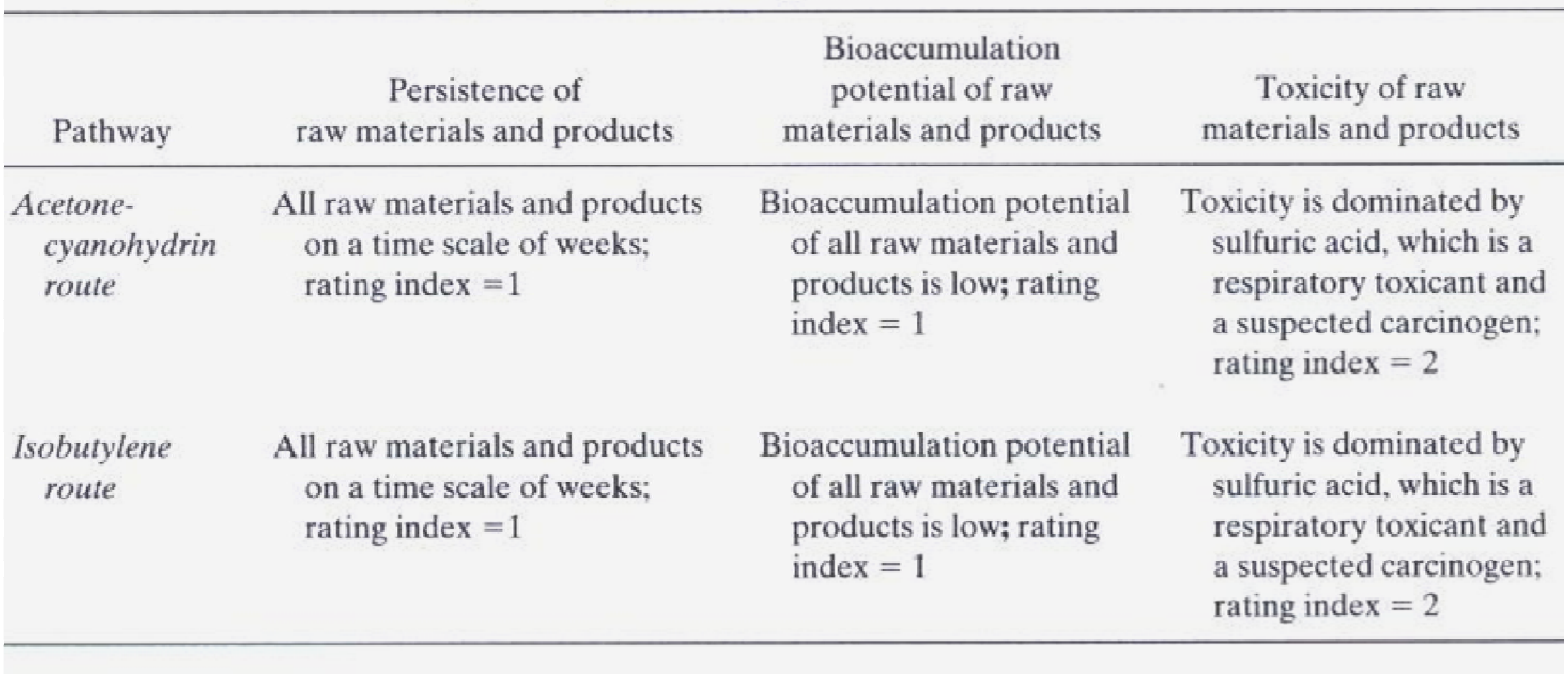
8.2.5 Evaluating Alternative Synthesis Pathways

Based on these criteria, the human toxicity concerns of the two MMA pathways would be dominated by the concerns associated with sulfuric acid. Thus two pathways would have 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 8.2-8 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 table.

Table 8.2-8 *Evaluation of methyl methacrylate 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
Acetone-cyanohydrin route	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
Isobutylene route	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

8.2.5 Evaluating Alternative Synthesis Pathways

To summarize, the environmental performance of the two pathways for manufacturing methyl methacrylate was evaluated based on economics, toxicity, and a combined assessment of persistence, bioaccumulation, and toxicity.

All of the approaches indicate a preference for the isobuthylene pathway. A similar case study with a different is given in Example 8.2-1.

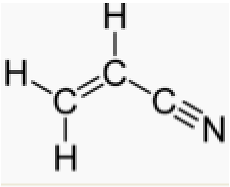
Example 8.2-1 Acrylonitrile Synthesis Pathways

Acrylonitrile can be produced via the ammoxidation of propylene or 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) Evaluation 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:

$C_2H_4 + HCN \rightarrow C_2H_4O$
$C_2H_4O + HCN \rightarrow HOC_2H_4CN \rightarrow C_3H_3N + H_2O$

Example 8.2-1 Acrylonitrile Synthesis Pathways

SOLUTION

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

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

The values for persistence and bioaccumulation were calculated using the EPISUITE^{TM} software package, which based on the methods described in Chapter 5.

Example 8.2-1 Acrylonitrile Synthesis Pathways

Table 8.2-9 Bioaccumulation and Persistence Data for Two Acrylonitrile Synthesis Routes

Compound	Persistence (atmospheric half life)	Aquatic half-life (Biodegradation index)	Bioaccumulation (Log BCF)
Ammoxidation of Propylene			
Propylene	**4.9 hours**	**weeks**	**4.6**
Ammonia	**NA**	**weeks**	**3.2**
Acrylonitrile	**30.5 hours**	**weeks**	**3.2**
HCN	**1 year**	**weeks**	**3.2**
Acetonitrile	**1 years**	**weeks**	**3.2**
Cyanation of ethylene oxide			
Ethylene	**15 hours**	**weeks**	**1.1**
HCN	**1 year**	**weeks**	**3.2**
Acrylonitrile	**30.5 hours**	**weeks**	**3.2**
CO_2	**—**	**—**	**—**

Example 8.2-1 Acrylonitrile Synthesis Pathways

Table 8.2-10 Stoichiometric, TLV, and Toxicity Weight Data for Two Acrylonitrile Synthesis Routes

Compound	Lb Produced Lb raw material per Lb Products	TLV (ppm)	Overall Inhalation toxicity factor	Overall oral toxicity factor
Ammoxidation of Propylene				
Propylene	**-1.1**	**>10,000**	**1**	**1**
Ammonia	**-0.4**	**25**	**100**	**100**
Acrylonitrile	**1**	**2**	**1,000**	**10,000**
HCN	**0.1**	**10**	**1,000**	**100**
Acetonitrile	**0.03**	**40**	**100**	**100**
Cyanation of ethylene oxide				
Ethylene	**-0.84**	**>10,000**	**1**	**1**
HCN	**-0.6**	**10**	**1,000**	**100**
Acrylonitrile	**1**	**2**	**1,000**	**10,000**
CO_2	**0.3**	**5,000**		

Example 8.2-1 Acrylonitrile Synthesis Pathways

(b) Evaluation 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.

For the **ammoxidation of propylene**, the environmental index based on the TLV and the index based EPA's toxicity weights are given by:

TLV Index = 1.1/10,000 + 0.4/25 + ½ + 0.1/10 + 0.03/40 = **0.53**
EPA Index = 1.1x1.0 + 0.4x100 + 1.0x10,000 + 0.1x1,000 + 0.03x100 = **10,144**

For the **cyanation of ethylene oxide**, the indices are:

TLV Index = 0.84/10,000 + 0.6/10 + ½ + 0.3/5000 = **0.56**
EPA Index = 0.84x1.0 + 0.6x1000 + 1.0x10,000 = **10,600**

The overall environmental performance of two pathway could be viewed as virtually identical (due to domination of acrylonitrile)

Example 8.2-1 Acrylonitrile Synthesis Pathways

Table 8.2-11 Stoichiometric, TLV, and Cost Data for Two Acrylonitrile Synthesis Routes

Compound	Stoichiometry	1/TLV (ppm)-1	Cost per pound
Ammoxidation of Propylene			
Propylene	**-1.1**	**1/10,000**	**$0.13**
Ammonia	**-0.4**	**1/25**	**$0.07**
Acrylonitrile	**1**	**1/2**	**$0.53**
HCN	**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**
HCN	**-0.6**	**1/10**	**$0.68**
Acrylonitrile	**1**	**½**	**$0.53**
CO_2	**0.3**	**1/5,000**	

Example 8.2-1 Acrylonitrile Synthesis Pathways

(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 x ($0.13) + 0.4 x ($0.07) = **$0.17**

Alternatively, an index could include raw material costs minus the value of salable byproducts:

Index = 1.1 x ($0.13) + 0.4 x ($0.07) – 0.1 x ($0.68) – 0.03 x ($0.65) = **$0.14**

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

Index = 0.84x0.23 + 0.6x$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.

Example 8.2-1 Acrylonitrile Synthesis Pathways

Environmental (Persistence and bioaccumulation) potential

(1) ammoxidation of propylene: relatively low persistence and bioaccumulation
(2) cyanation of ethylene oxide: relatively low persistence and bioaccumulation

Economic index

(1) ammoxidation of propylene: \$0.14
(2) cyanation of ethylene oxide: \$0.60

Toxicity potential

(1) ammoxidation of propylene: TLV Index = 0.53, EPA Index = 10,144
(2) cyanation of ethylene oxide: TLV Index = 0.56, EPA Index = 10,600

8.3 Tier 2 Environmental Performance Tools

Once the basic input-output structure of a flow sheet is determined, a preliminary process flowsheet is developed. Typically, storage devices, reactors, and separation devices might be identified, and some information would be available about equipment sizes or process stream flow rates. This level of process specification is an appropriate time to re-examine environmental performance.

At this stage of analysis, it still may be necessary to screen large numbers of design alternatives, but more information about the process is available and should be incorporated into the environmental performance evaluation.

8.3 Tier 2 Environmental Performance Tools

This section describes methods for performing environmental evaluation at this intermediate level. A first step in this analysis is to use the information available on the process units to estimate the magnitude and composition of emissions and wastes. Some of these emissions estimation tools are described in Section 8.3.1.

Once the emissions, wastes, and other process flow are characterized, any of a number of environmental performance evaluation methods can be employed. Environmental performance evaluation tools, suitable for this level of analysis, are described in Section 8.3.2.

8.3 Tier 2 Environmental Performance Tools

8.3.1 Environmental Release Assessment

8.3.1.1 Basics of Releases

- Release include any spilling, leaking, pumping, pouring, emitting, emptying, discharging, injecting, escaping, leaching, dumping, disposing into environment of any chemical

- Term ‘environment’ includes water, air and land, the three media to which release may occur

- Related to releases are transfers of chemical wastes off-site for purpose other than making a salable product. Such purposes could include treatment or disposal.

8.3.1 Environmental Release Assessment

Release assessments are documents contain information on release rates, frequencies, media of releases, and others. Steps required in making release assessment are:

1. Identify purpose and need for release assessment
2. Obtain or diagram a process flowsheet
3. Identify and list waste and emissions streams
4. Examine the flowsheet for additional waste and emission streams
5. For each release point identified in steps 3 and 4, determine the best available method for quantifying the release rate
6. Determine data or information needed to use the quantification methods determined in step 5
7. Collect data and information to fill gaps
8. Quantify the chemical’s release rates and frequencies and the media to which release occur
9. Document the assessment, include a characterization of uncertainties

8.3.1 Environmental Release Assessment

A release assessment begins after one or more processes have been selected for analysis. At this point, the basic features (e.g., mass balances, unit operations and operating conditions) of design are available. A flow diagram showing process stream is often a key tool in beginning the analysis. From the flow diagram, process output streams that are not usable can be identified as potential releases.

Some potential releases cannot be identified for various reasons;

- some are not directly attributable to process equipments
- some result from process inefficiencies
- some may be infrequent
- some may be difficult to quantify
- some may be overlooked

8.3.1 Environmental Release Assessment

Common sources of releases that are often missing in flow sheet

- fugitive emissions (leaks)
- venting of equipment (e.g., breathing and displacement losses, etc.)
- periodic equipment cleaning (may be frequent or infrequent)
- transport container residuals (e.g., from drums, totes, tank trucks, rail cars, barges)
- incomplete separations (e.g., distillation, phase separation, filtrations, etc.)

Fugitive: 고정되지 않는, 붙잡기 어려운, 날아가는 것

8.3.1 Environmental Release Assessment

The manner in which a chemical is released is a crucial factor in assessing environmental impact. In characterizing manner in which a chemical is released, it is convenient to first determine whether the release is expected to occur *on-site* or from some extension of the site to an *off-site* location, such as a pipe extending into a water body.

On-site releases to the environment include emission to the air, discharges to surface waters, and releases to land and underground injection wells. Both routine releases, such as fugitive air emissions and accidental or non-routine releases, such as chemical spills, are part of on site releases.

8.3.1 Environmental Release Assessment

On-site releases do not include transfers or shipments of chemicals from the facility for sale or distribution in commerce, or of wastes to other facilities for disposal, treatment, energy recovery. Chemical wastes that are transferred or shipped to an off-site location, such as a publicly owned treatment works (POTW), where the waste may be fully or partially released, are called **“off-site transfer”**

Once emissions and wastes have been characterized as on-site or off-site, the on-site releases are classified by the medium or media to which the chemical is released. Releases to common classes of media are described below.

8.3.1 Environmental Release Assessment

✿ Air releases (emissions)

Primary emissions occurs as a direct consequence of the production or use within process. These emissions may come from either point source (stack) or non-point source (fugitive).

Stack releases occur through vents, ducts, pipes, or other confined gas streams. Stack releases include storage tank and unit operation vent emissions and, generally, air releases from air pollution control equipment. Unit operations of importance as emission sources include pressure relief vents on reactors, and vents on distillation column condensers, absorption and stripping columns vent, and feed or product storage tank vents.

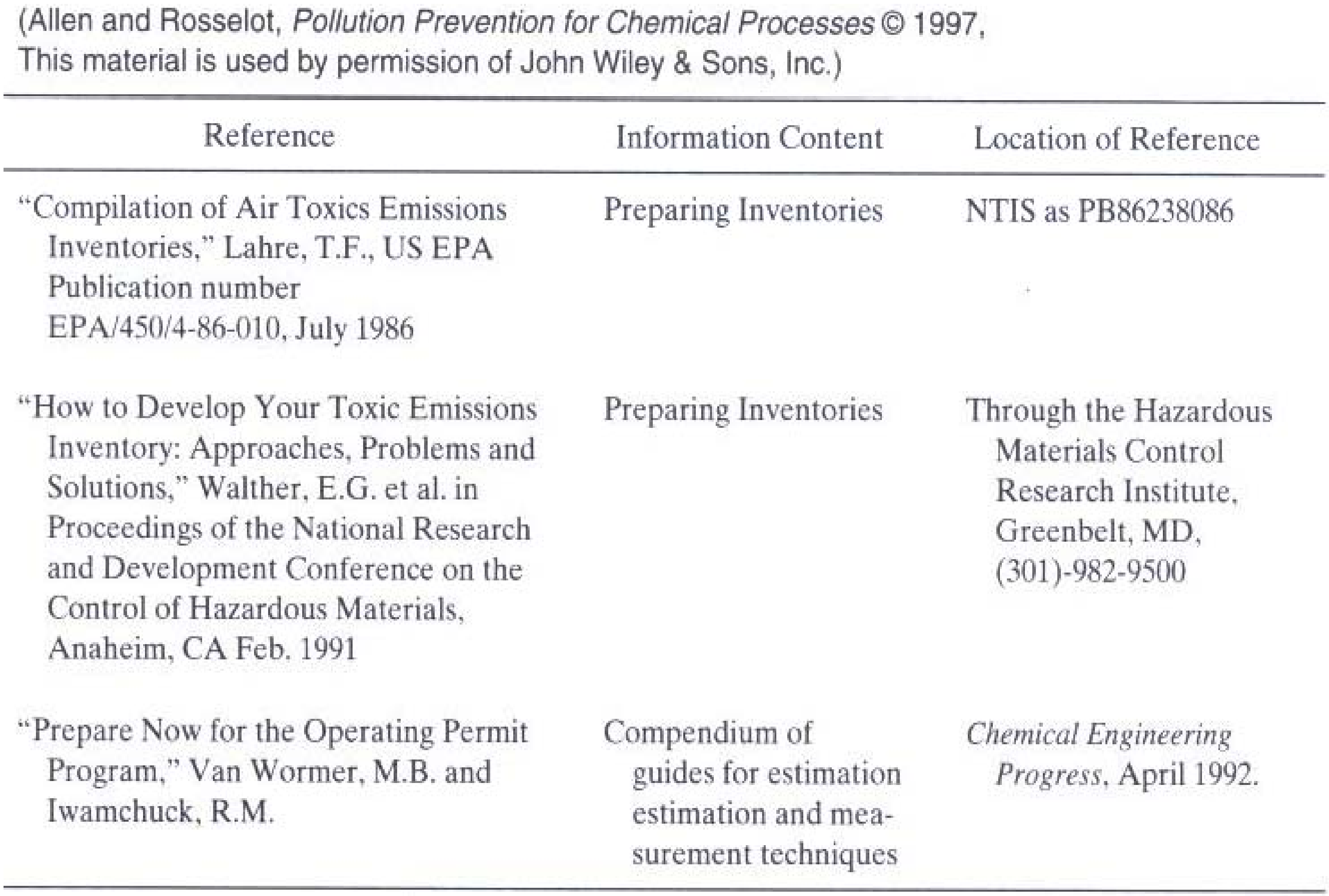
8.3.1 Environmental Release Assessment

Fugitive air emissions are not releases through stacks, vents, ducts, pipes, or any other confined gas streams. These releases include fugitive equipment leaks from valve, pump seals, flanges, compressors, sampling connections, open-ended lines, etc.; releases from building ventilation systems; and any other fugitive or non-point air emissions. Fugitive emissions occur from process sources that are not easily identifiable and are of relatively large number within the process.

Secondary emissions occurs indirectly as a result of the production or use of a specific compound. These emission sources include utility consumptions, evaporative losses from surface impoundment and spills, and industrial wastewater collection systems.

Because emissions to air can be difficult to measure and emission sources can be difficult to locate, some resources for preparing plat-wide emission inventories have been developed. Several references for secondary release resources in **Table 8.3-1.**

Table 8.3-1
Resources for preparing plant-wide emission inventories



(Allen and Rosselot, *Pollution Prevention for Chemical Processes* © 1997,
This material is used by permission of John Wiley & Sons, Inc.)

Reference	Information Content	Location of Reference
"Compilation of Air Toxics Emissions Inventories," Lahre, T.F., US EPA Publication number EPA/450/4-86-010, July 1986	Preparing Inventories	NTIS as PB86238086
"How to Develop Your Toxic Emissions Inventory: Approaches, Problems and Solutions," Walther, E.G. et al. in Proceedings of the National Research and Development Conference on the Control of Hazardous Materials, Anaheim, CA Feb. 1991	Preparing Inventories	Through the Hazardous Materials Control Research Institute, Greenbelt, MD, (301)-982-9500
"Prepare Now for the Operating Permit Program," Van Wormer, M.B. and Iwamchuck, R.M.	Compendium of guides for estimation estimation and measurement techniques	*Chemical Engineering Progress*, April 1992.

Compendium : 개요

8.3.1 Environmental Release Assessment

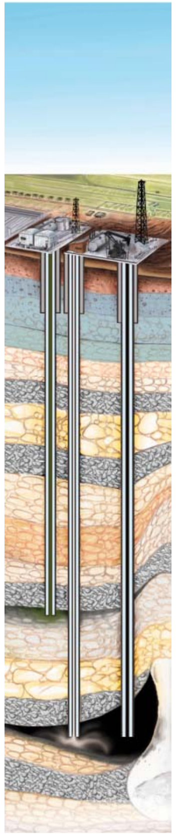
❁ Water Releases

Releases of chemicals from discharge points in a process can be to a receiving stream or water body. Theses are include process outfalls such as pipes and open trenches, releases from on-site wastewater treatment systems, and the contribution from storm-water runoff. Water releases do not include discharges to a POTW or other off-site wastewater treatment facilities. These are off-site transfer.

8.3.1 Environmental Release Assessment

Underground Injection Releases

Some chemicals may be injected into wells at a facility. US EPA regulations apply to underground wells, which are classified by the type of material injected into the well. The Underground Injection Control Program of the Federal Safe Drinking Water Act is found in 40 CFR part 144-147.



8.3.1 Environmental Release Assessment

❀ Release to Land

Some chemicals may be released to land within the boundaries of a facility. Some facilities may have on-site landfills for chemical disposal. Land treatment/application farming is a disposal method in which a waste containing chemical is applied onto or incorporated into soil. While this disposal method is considered a release to land, any volatilization of chemicals into the air occurring during the disposal operation is a fusitive air release.

Chemicals may also be disposed to a surface impoundment. A surface impoundment is a natural topographic depression, man-made excavation, or diked area formed primarily of earthen materials that is designed to hold an accumulation of liquid wastes or wastes containing free liquids. Example of surface impoundments are holding, settling, storage, and elevation pits; ponds; and lagoons. If the pit or pond is intended for storage, it would be considered to be surface impoundment used as a final disposal method.

8.3.2 Release Quantification Methods

General hierarchy of order of preference for quantifying releases

a. Measured release data for chemical or indirectly measured release data using mass balance or stoichiometric ratios

b. Release data for a surrogate chemical with similar release-affecting properties and used in the same process (some emission factors be considered to be surrogate data).

c. Modeled release estimates:

- mathematically modeled release estimates for the chemical
- rule-of-thumb release estimates, or those developed using engineering judgment

8.3.2 Release Quantification Methods

8.3.2.1 Measured Release Data for the Chemical

- How data may be used to generate estimates of release?

  For continuous process : a release can be estimated by calculating the product of three measures:

(1) a chemical's average concentration

(2) average volumetric flow rate of the release stream containing chemical

(3) density of the release stream

(Example 8.3-1)

8.3.2 Release Quantification Methods

Example 8.3-1

A wastewater pretreatment plant runs every day and averages 1.5 million gallons per day. The following chromium concentrations were measured. How much chromium dose the POTW receive annually?

Sample #	1	2	3	4	5	6	7
Cr(III) [ppm]	2.7	0.9	4.1	3.4	5.1	2.3	3.8

Solution:

average Cr(III) concentration =3.2 mg/kg

Effluent=1,500,000 gal/day x 3.78 kg/gal = 5,670,000 kg/day

Annual estimate

= 5,670,000 kg/day effluent x 3.2 kg Cr(III)/1,000,000 kg effluent x 365 days/yr

=6,600 kg/yr Cr(III)

8.3.2 Release Quantification Methods

8.3.2.2 Release data for a Surrogate Chemical

Release data for analogous or surrogate chemicals from existing processes can sometimes be used to estimate releases of chemical of interest in processes in design or in existing processes. To use surrogate chemical data, similarities must exist in some physical/chemical properties of the chemicals, unit processes and their operating conditions, and quantities of chemical throughput.

For instance, in Ex 8.3-1, if an estimate of the release rate for Cr(VI), which is a different oxidation state of chromium than Cr(III), was desired, then Cr(III) might be used as a surrogate. If data were available indicating that a typical ratio of Cr(III) to Cr(VI) were 1000:1, then the release rate of Cr(VI) might be estimated.

8.3.2 Release Quantification Methods

8.3.2.3 Emission factors

- **Emission factors** are commonly used to estimate releases to air. A number of unit operation-specific emission factor databases have been complied for the US EPA.

- Data bases (AP-42) for emission factor have been compiled by the US EPA-NAAQS (National Ambient Air Quality Standards as SO_2, NO_2, CO, O_3, hydrocarbons, particulates)

- For several industrial sectors
  - unit-by-unit (reactors, separation columns, storage tanks, etc.)
  - **location and estimation** of air emissions from sources (**L&E**)

Emission factor

US EPA, Compilation of Air Pollution Emission factors, Volume I: “Stationary point and area sources”, 4th edition, with Supplements A-D, US Environmental Protection Agency, Research Triangle Park, NC, Publication **AP-42**, 1985

The most recent and comprehensive emission factor document from the US EPA is titled the *Factor Information Retrieval (FIRE) system*. It contains EPA’s recommended criteria and hazardous air pollution (HAP) emission estimation factors.

8.3.2.4 Emissions from Process Units and Fugitive Sources

Rate of Emission (E, mass/time) of VOC from unit operations:

$$E = (m_{VOC})(EF_{av})(M)$$

where

m_{VOC} : mass fraction of VOC in the stream or process unit

EF_{av} : the average emission factor ascribed to that stream or process unit (kg emitted/10^3 kg throughput)

M : mass flow rate through the unit (mass/time)

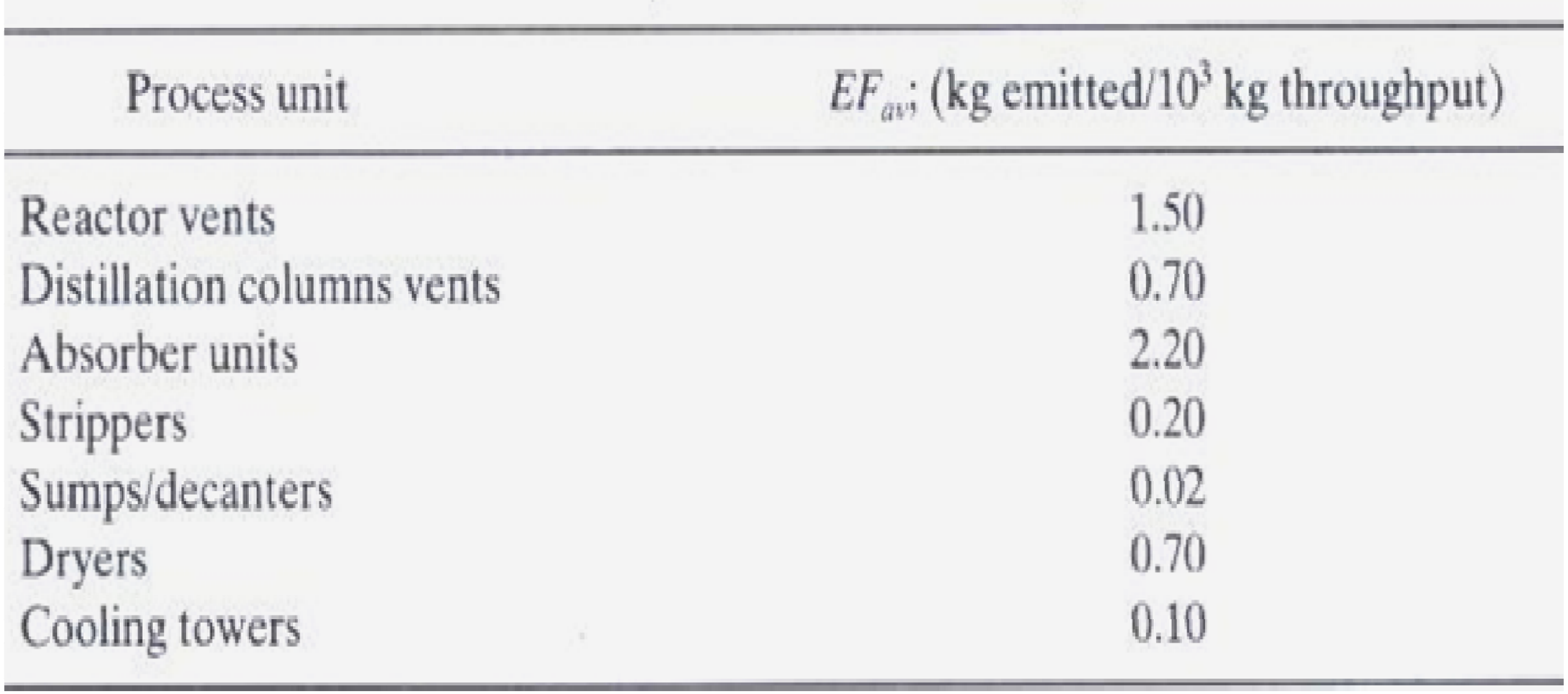
Table 8.3-2 : average emission factors by US EPA

Table 8.3-3 : emission factors for fugitive sources in various plants

Examples 8.3-2, 8.3-3

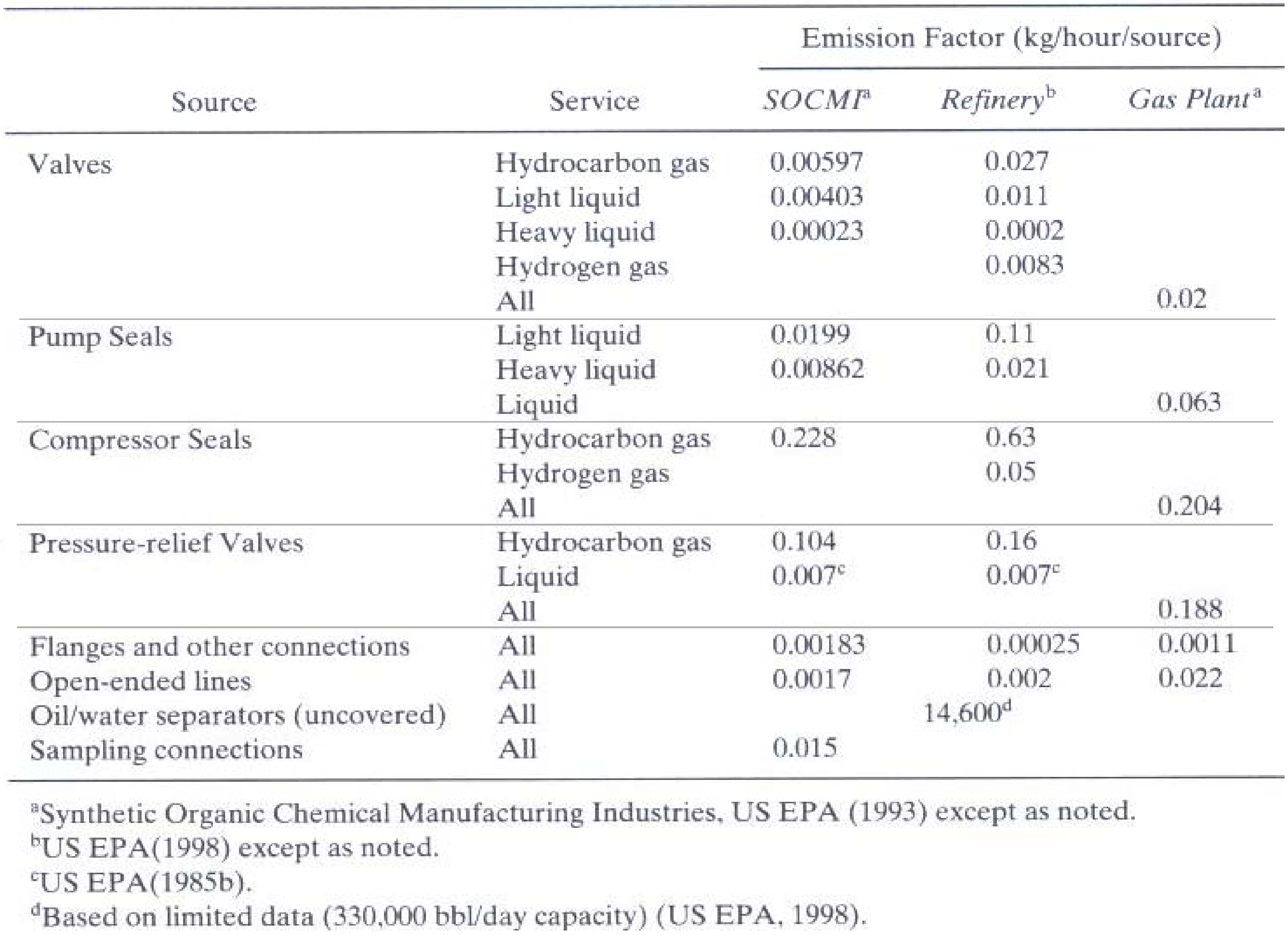
Table 8.3-2

Average emission factors for chemical process units calculated from the EPA Locating & Estimating Air Emissions from Sources (L&E) database (Shonnard, 1995)



Process unit	EF_{av}; (kg emitted/10^3 kg throughput)
Reactor vents	1.50
Distillation columns vents	0.70
Absorber units	2.20
Strippers	0.20
Sumps/decanters	0.02
Dryers	0.70
Cooling towers	0.10

Table 8.3-3 average emission factors for estimating fugitive emissions



Source	Service	Emission Factor (kg/hour/source)		
		SOCMI[a]	*Refinery*[b]	*Gas Plant*[a]
Valves	Hydrocarbon gas	0.00597	0.027	
	Light liquid	0.00403	0.011	
	Heavy liquid	0.00023	0.0002	
	Hydrogen gas		0.0083	
	All			0.02
Pump Seals	Light liquid	0.0199	0.11	
	Heavy liquid	0.00862	0.021	
	Liquid			0.063
Compressor Seals	Hydrocarbon gas	0.228	0.63	
	Hydrogen gas		0.05	
	All			0.204
Pressure-relief Valves	Hydrocarbon gas	0.104	0.16	
	Liquid	0.007[c]	0.007[c]	
	All			0.188
Flanges and other connections	All	0.00183	0.00025	0.0011
Open-ended lines	All	0.0017	0.002	0.022
Oil/water separators (uncovered)	All		14,600[d]	
Sampling connections	All	0.015		

[a] Synthetic Organic Chemical Manufacturing Industries, US EPA (1993) except as noted.

[b] US EPA(1998) except as noted.

[c] US EPA(1985b).

[d] Based on limited data (330,000 bbl/day capacity) (US EPA, 1998).

8.3.2.5 Losses of Residuals from Cleaning of Drums and Tanks

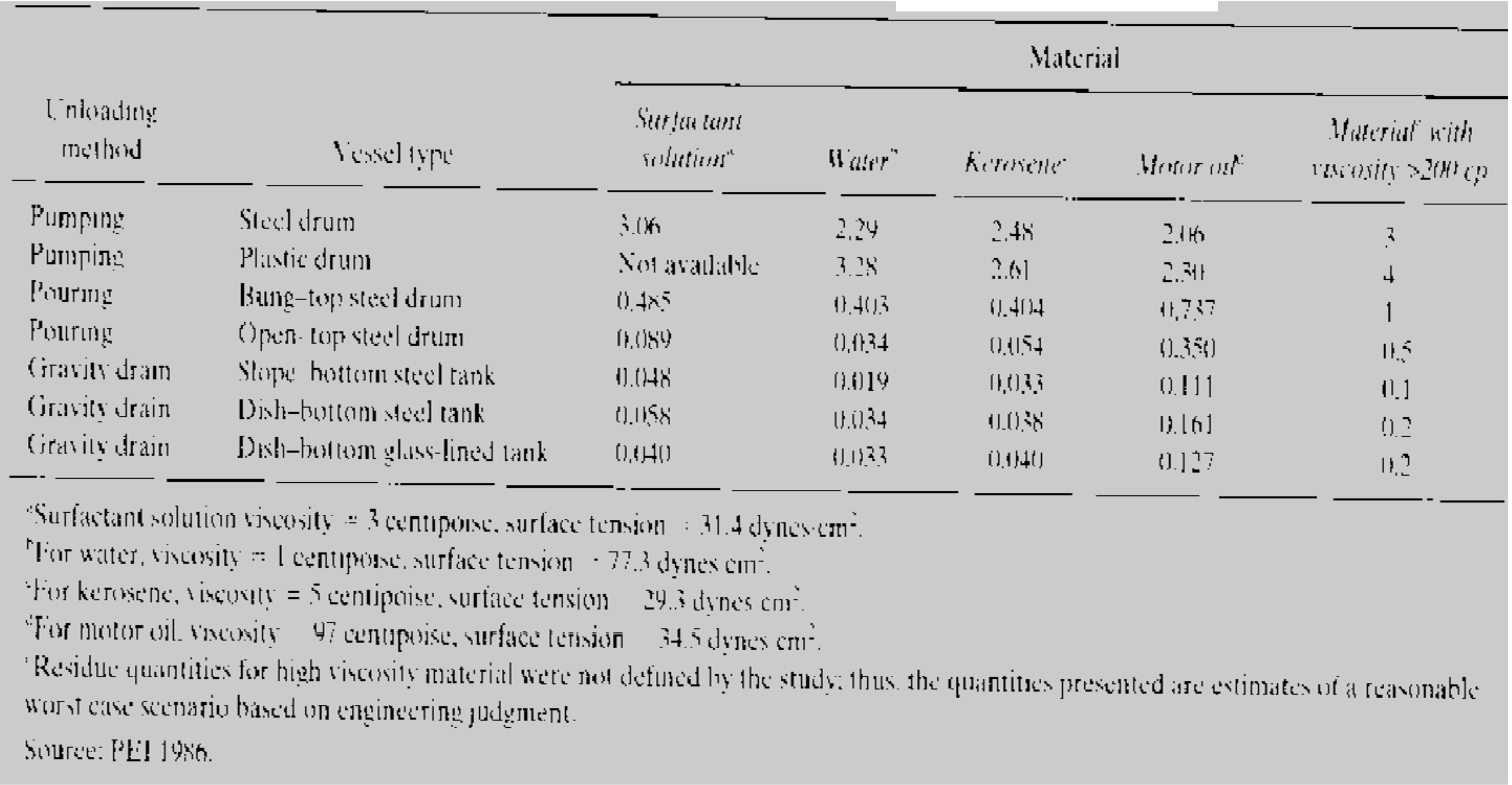
Nature of Cleaning Process should be considered

- capacity, shape and material of vessel construction
- cleaning schedule, residual quantities of chemicals in the vessels
- type and amount of solvent (batch volume)
- solubility/miscibility of the chemicals in the solvent
- any treatment of wastewater containing the chemical, etc.

Table 8.3-4 presents factors for estimating % chemical remaining in drums and tanks after unloading. These factors were derived from a pilot scale research project

Table 8.3-4

Residual quantities from pilot-plant experimental study (wt%)



Unloading method	Vessel type	Material				
		Surfactant solution[a]	*Water*[b]	*Kerosene*[c]	*Motor oil*[d]	*Material*[e] *with viscosity >200 cp*
Pumping	Steel drum	3.06	2.29	2.48	2.06	3
Pumping	Plastic drum	Not available	3.28	2.61	2.30	4
Pouring	Bung–top steel drum	0.485	0.403	0.404	0.737	1
Pouring	Open- top steel drum	0.089	0.034	0.054	0.350	0.5
Gravity drain	Slope bottom steel tank	0.048	0.019	0.033	0.111	0.1
Gravity drain	Dish–bottom steel tank	0.058	0.034	0.038	0.161	0.2
Gravity drain	Dish–bottom glass-lined tank	0.040	0.033	0.040	0.127	0.2

[a] Surfactant solution viscosity = 3 centipoise, surface tension = 31.4 dynes·cm^{-2}.

[b] For water, viscosity = 1 centipoise, surface tension = 77.3 dynes cm^{-2}.

[c] For kerosene, viscosity = 5 centipoise, surface tension = 29.3 dynes cm^{-2}.

[d] For motor oil, viscosity = 97 centipoise, surface tension = 34.5 dynes cm^{-2}.

[e] Residue quantities for high viscosity material were not defined by the study; thus, the quantities presented are estimates of a reasonable worst case scenario based on engineering judgment.

Source: PEI 1986.

8.3.2.6 Secondary Emissions from Utility Sources

Utility consumption in chemical processes is a larger generator of environmental impact. Emission factor for uncontrolled release for residual and distillate oil combustion (**Table 8.3-5).** Emission factor for combustion of natural gas **(Table 8.3-6)**

Emissions for fuel and natural gas combustion

$$E\ (\mathrm{kg/unit/yr}) = (ED)(EF)(FV)^{-1}(BE)^{-1}$$

ED : energy demand of a unit process (energy demand/unit/yr)

EF : emission factor for the fuel type (kg/volume of fuel combusted)

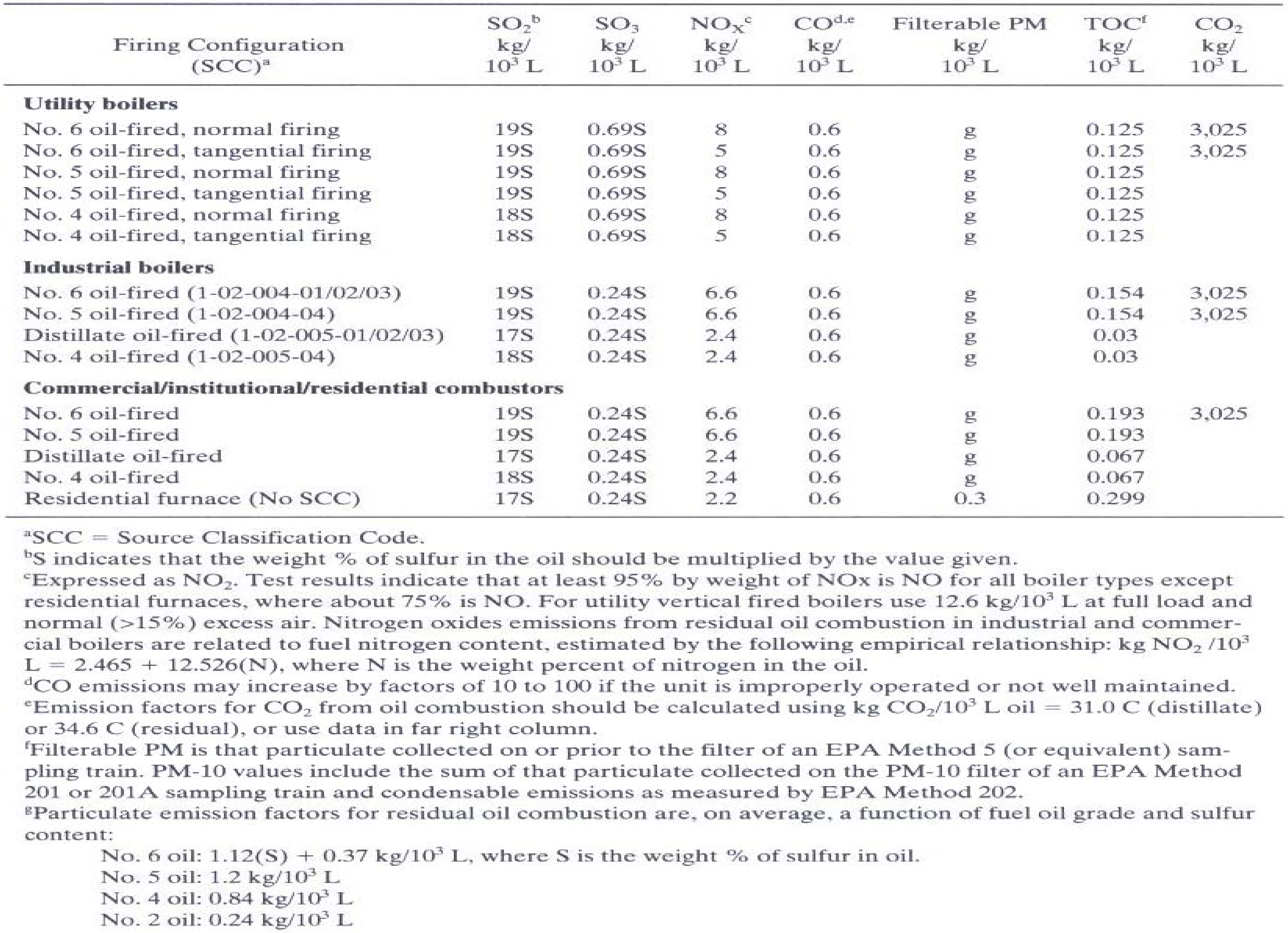
BE : boiler efficiency (unitless; 0.75-0.90 is a typical range of values)

FV : fuel value (energy/volume fuel combusted)

typical heating value for solid, liquid and gas **(Table 8.3-7)**

Table 8.3-5

Critical pollutant emission factors(EF) for uncontrolled releases from residual and distillate oil combustion



Firing Configuration (SCC)[a]	SO_2[b] kg/ 10^3 L	SO_3 kg/ 10^3 L	NO_X[c] kg/ 10^3 L	CO[d,e] kg/ 10^3 L	Filterable PM kg/ 10^3 L	TOC[f] kg/ 10^3 L	CO_2 kg/ 10^3 L
Utility boilers							
No. 6 oil-fired, normal firing	19S	0.69S	8	0.6	g	0.125	3,025
No. 6 oil-fired, tangential firing	19S	0.69S	5	0.6	g	0.125	3,025
No. 5 oil-fired, normal firing	19S	0.69S	8	0.6	g	0.125	
No. 5 oil-fired, tangential firing	19S	0.69S	5	0.6	g	0.125	
No. 4 oil-fired, normal firing	18S	0.69S	8	0.6	g	0.125	
No. 4 oil-fired, tangential firing	18S	0.69S	5	0.6	g	0.125	
Industrial boilers							
No. 6 oil-fired (1-02-004-01/02/03)	19S	0.24S	6.6	0.6	g	0.154	3,025
No. 5 oil-fired (1-02-004-04)	19S	0.24S	6.6	0.6	g	0.154	3,025
Distillate oil-fired (1-02-005-01/02/03)	17S	0.24S	2.4	0.6	g	0.03	
No. 4 oil-fired (1-02-005-04)	18S	0.24S	2.4	0.6	g	0.03	
Commercial/institutional/residential combustors							
No. 6 oil-fired	19S	0.24S	6.6	0.6	g	0.193	3,025
No. 5 oil-fired	19S	0.24S	6.6	0.6	g	0.193	
Distillate oil-fired	17S	0.24S	2.4	0.6	g	0.067	
No. 4 oil-fired	18S	0.24S	2.4	0.6	g	0.067	
Residential furnace (No SCC)	17S	0.24S	2.2	0.6	0.3	0.299	

[a] SCC = Source Classification Code.

[b] S indicates that the weight % of sulfur in the oil should be multiplied by the value given.

[c] Expressed as NO_2. Test results indicate that at least 95% by weight of NOx is NO for all boiler types except residential furnaces, where about 75% is NO. For utility vertical fired boilers use 12.6 kg/10^3 L at full load and normal (>15%) excess air. Nitrogen oxides emissions from residual oil combustion in industrial and commercial boilers are related to fuel nitrogen content, estimated by the following empirical relationship: kg NO_2 /10^3 L = 2.465 + 12.526(N), where N is the weight percent of nitrogen in the oil.

[d] CO emissions may increase by factors of 10 to 100 if the unit is improperly operated or not well maintained.

[e] Emission factors for CO_2 from oil combustion should be calculated using kg CO_2/10^3 L oil = 31.0 C (distillate) or 34.6 C (residual), or use data in far right column.

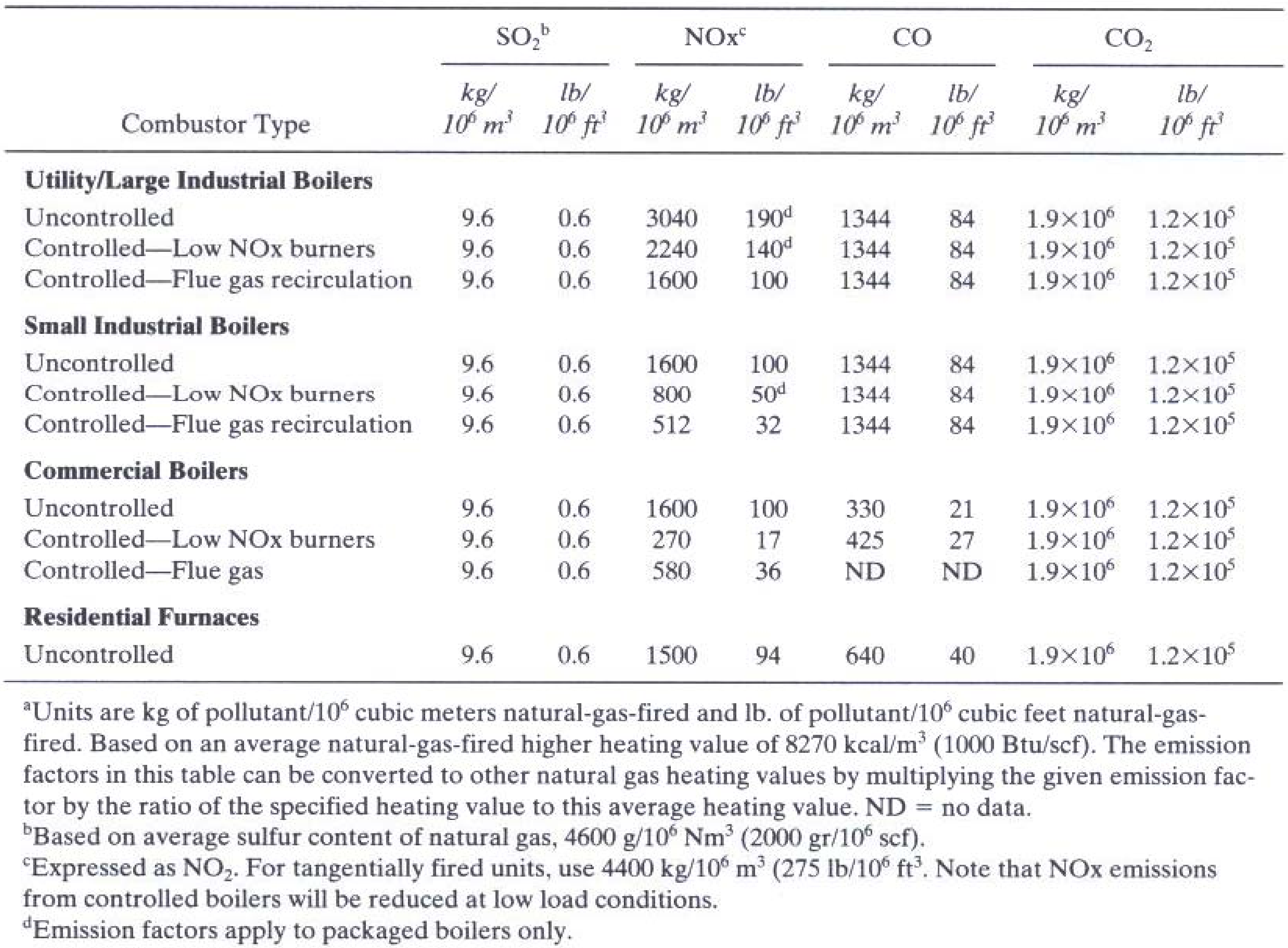
[f] Filterable PM is that particulate collected on or prior to the filter of an EPA Method 5 (or equivalent) sampling train. PM-10 values include the sum of that particulate collected on the PM-10 filter of an EPA Method 201 or 201A sampling train and condensable emissions as measured by EPA Method 202.

[g] Particulate emission factors for residual oil combustion are, on average, a function of fuel oil grade and sulfur content:

No. 6 oil: 1.12(S) + 0.37 kg/10^3 L, where S is the weight % of sulfur in oil.
No. 5 oil: 1.2 kg/10^3 L
No. 4 oil: 0.84 kg/10^3 L
No. 2 oil: 0.24 kg/10^3 L

Table 8.3-6

Emission factors for SO_2, NO_x, CO from Natural Gas Combustion



Combustor Type	SO_2[b]		NOx[c]		CO		CO_2	
	kg/ 10^6 m^3	*lb/ 10^6 ft^3*	*kg/ 10^6 m^3*	*lb/ 10^6 ft^3*	*kg/ 10^6 m^3*	*lb/ 10^6 ft^3*	*kg/ 10^6 m^3*	*lb/ 10^6 ft^3*
Utility/Large Industrial Boilers								
Uncontrolled	9.6	0.6	3040	190[d]	1344	84	1.9×10^6	1.2×10^5
Controlled—Low NOx burners	9.6	0.6	2240	140[d]	1344	84	1.9×10^6	1.2×10^5
Controlled—Flue gas recirculation	9.6	0.6	1600	100	1344	84	1.9×10^6	1.2×10^5
Small Industrial Boilers								
Uncontrolled	9.6	0.6	1600	100	1344	84	1.9×10^6	1.2×10^5
Controlled—Low NOx burners	9.6	0.6	800	50[d]	1344	84	1.9×10^6	1.2×10^5
Controlled—Flue gas recirculation	9.6	0.6	512	32	1344	84	1.9×10^6	1.2×10^5
Commercial Boilers								
Uncontrolled	9.6	0.6	1600	100	330	21	1.9×10^6	1.2×10^5
Controlled—Low NOx burners	9.6	0.6	270	17	425	27	1.9×10^6	1.2×10^5
Controlled—Flue gas	9.6	0.6	580	36	ND	ND	1.9×10^6	1.2×10^5
Residential Furnaces								
Uncontrolled	9.6	0.6	1500	94	640	40	1.9×10^6	1.2×10^5

[a] Units are kg of pollutant/10^6 cubic meters natural-gas-fired and lb. of pollutant/10^6 cubic feet natural-gas-fired. Based on an average natural-gas-fired higher heating value of 8270 kcal/m^3 (1000 Btu/scf). The emission factors in this table can be converted to other natural gas heating values by multiplying the given emission factor by the ratio of the specified heating value to this average heating value. ND = no data.

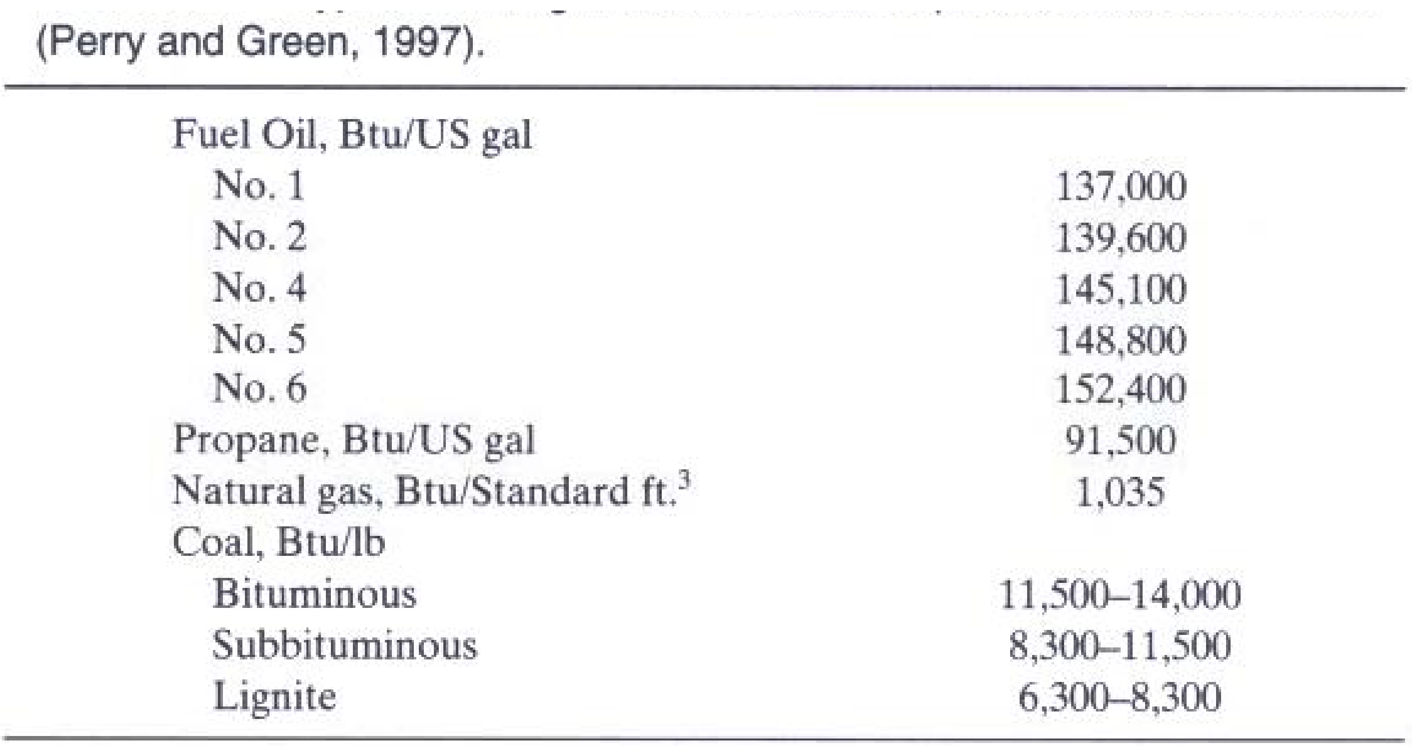
[b] Based on average sulfur content of natural gas, 4600 g/10^6 Nm^3 (2000 gr/10^6 scf).

[c] Expressed as NO_2. For tangentially fired units, use 4400 kg/10^6 m^3 (275 lb/10^6 ft^3. Note that NOx emissions from controlled boilers will be reduced at low load conditions.

[d] Emission factors apply to packaged boilers only.

Table 8.3-7

Typical heating value for solid, liquid and gas fuels



(Perry and Green, 1997).

Fuel Oil, Btu/US gal	
No. 1	137,000
No. 2	139,600
No. 4	145,100
No. 5	148,800
No. 6	152,400
Propane, Btu/US gal	91,500
Natural gas, Btu/Standard ft.^{3}	1,035
Coal, Btu/lb	
Bituminous	11,500–14,000
Subbituminous	8,300–11,500
Lignite	6,300–8,300

8.3.2.6 Secondary Emissions from Utility Sources

Emissions from electricity consumption in processes

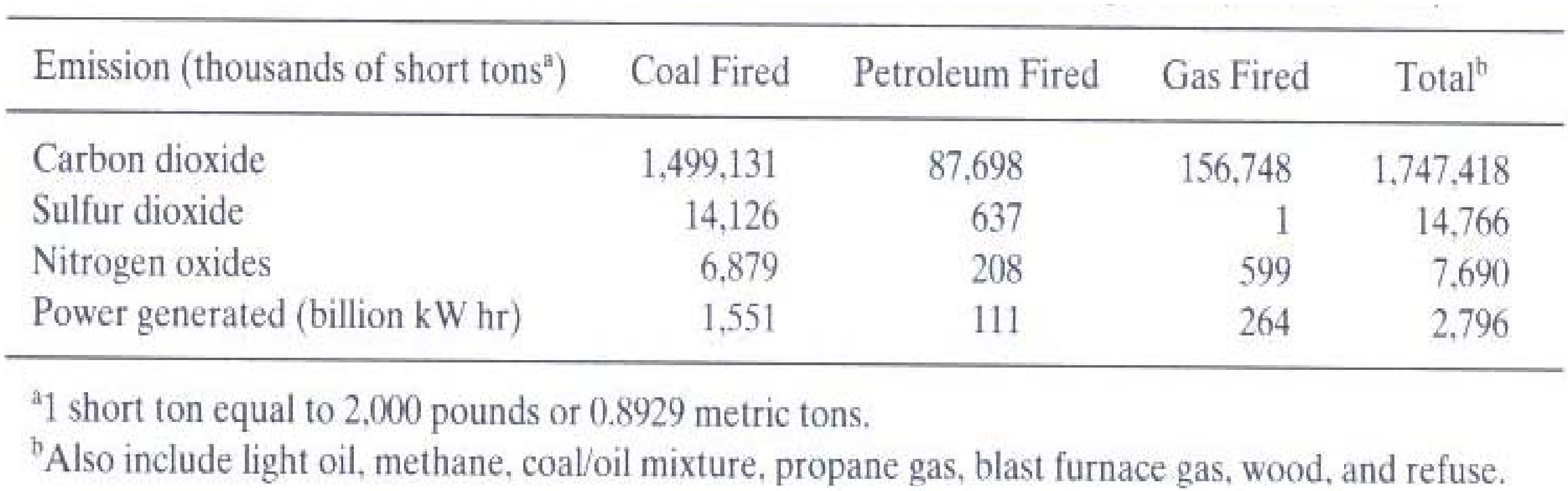
$$E\ (\text{kg/unit/yr}) = (\text{ED})(\text{EF})(\text{ME})^{-1}$$

where ED : electricity demand of unit per year
ME : efficiency of the device

(Table 8.3-8)

Table 8.3-8

Emission from fossil-fuel steam electric generating units



Emission (thousands of short tons[a])	Coal Fired	Petroleum Fired	Gas Fired	Total[b]
Carbon dioxide	1,499,131	87,698	156,748	1,747,418
Sulfur dioxide	14,126	637	1	14,766
Nitrogen oxides	6,879	208	599	7,690
Power generated (billion kW hr)	1,551	111	264	2,796

[a] 1 short ton equal to 2,000 pounds or 0.8929 metric tons.

[b] Also include light oil, methane, coal/oil mixture, propane gas, blast furnace gas, wood, and refuse.

8.3.3 Modeled Release Estimates

Guidance and methods for calculating some of the release points not normally included in process design software and conventional methods

Loading Transport Containers

- AP- 42 **(Appendix F)** document on estimation methods
- loading losses are a primary source of evaporative emissions from rail tank car, truck and similar operations
- quantity of evaporative loss from loading operation is a function of
  - physical and chemical characteristics of the previous cargo
  - method of unloading the previous cargo
  - operations to transport the empty carrier to a loading terminal
  - method of loading the new cargo
  - physical and chemical characteristics of the new cargo

8.3.3 Modeled Release Estimates

- principal methods of cargo carrier loading
  - splash loading method ***(Fig. 8.3-1)***
  - submerged fill pipe ***(8.3-2)***
  - bottom loading ***(8.3-3)***

- control measure for vapors displaced during liquid unloeading ***(Fig. 8.3-4)***

Splash Loading Method

In splash loading method, the fill pipe dispensing the cargo is lowered only part way into the cargo tank. Significant turbulence and vapor/liquid contact occur during the splash loading operation, resulting in droplets will be entrained in the vented vapors.

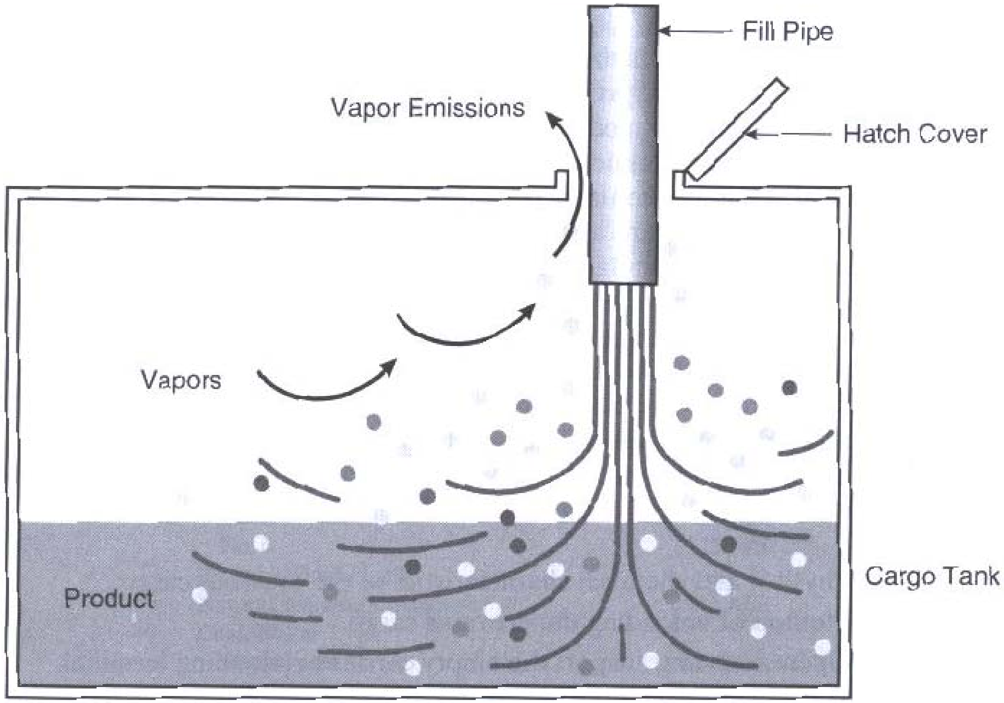


Fig. 8.3-1 Splash loading method

Submerged Loading Method

In Submerged loading method, the fill pipe opening is below the liquid surface level. Liquid turbulence is controlled significantly during submerged loading, resulting in much lower vapor generation than encountered during splash loading.

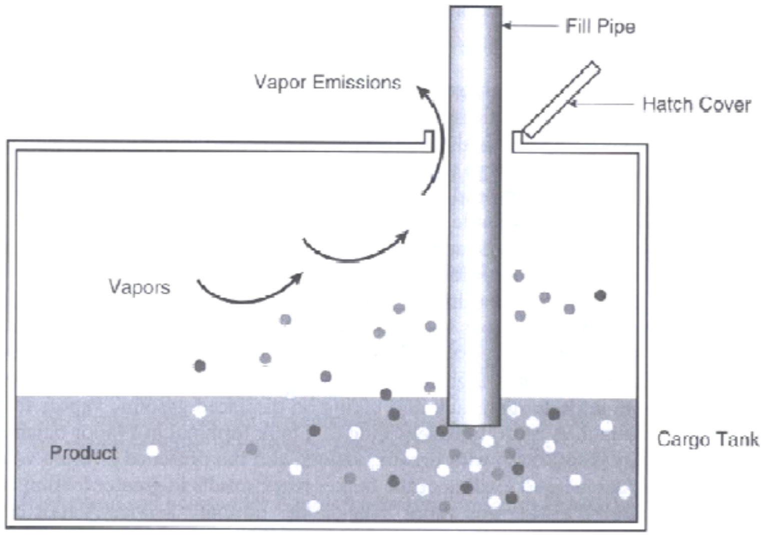


Fig. 8.3-2 Submerged fill pipe: the fill pipe extends almost to the bottom of the cargo tank.

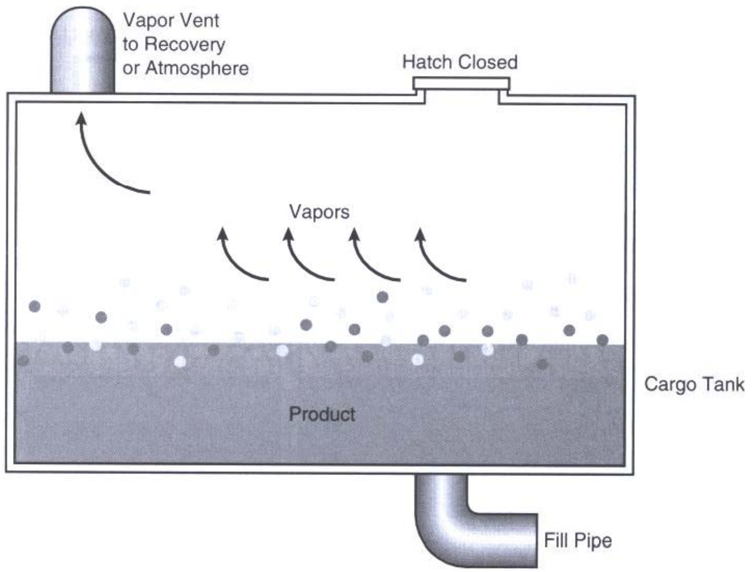


Fig. 8.3-3 Bottom loading: a permanent fill pipe is attached to the cargo tank bottom

Cargo carrier

The recent loading history of a cargo carrier is just as important a factor in loading losses as the method of loading. If the cargo carrier has carried a nonvolatile liquid such as fuel oil, or has just been cleaned, it will contain vapor-free air. If it has just carried gasoline and has not been vented, the air in the carrier tank contain volatile organic vapors, which will be expelled during the loading operation along with newly generated vapors.

Cargo carriers are sometimes designated to transport only one product, and in such cases are practicing “dedicated service.” Dedicated gasoline cargo tanks return to a loading terminal containing air fully or partially saturated with vapor from the previous load. Cargo tanks may also be “switch loaded” with various products, so that a nonvolatile product being loaded may expel the vapors remaining from a previous load of a volatile product such as gasoline.

dedicated service: 전용

Tank truck in vapor balancing service

One control measure for vapors displaced during liquid unloading at bulk plants or service stations is called "vapor balance service". The cargo tank on the truck retrieves the vapors displaced, then the truck transports the vapors back to loading terminal. Figure 8.3-4 shows a tank truck in "vapor balance service" filling an underground tank and taking on displaced gasoline vapors for return to the terminal. A cargo tank returning to a bulk terminal in "vapor balance service" normally is saturated with organic vapors, and presence of these vapors at the start of submerged loading of the tanker truck results in greater loading losses than encounted during non-vapor balance, or "normal service". Vapor balance service is usually not practiced with marine vessels, although some vessels practice emission control by means of vapor transfer within their own cargo tanks during ballasting operations.

Tank truck in vapor balancing service

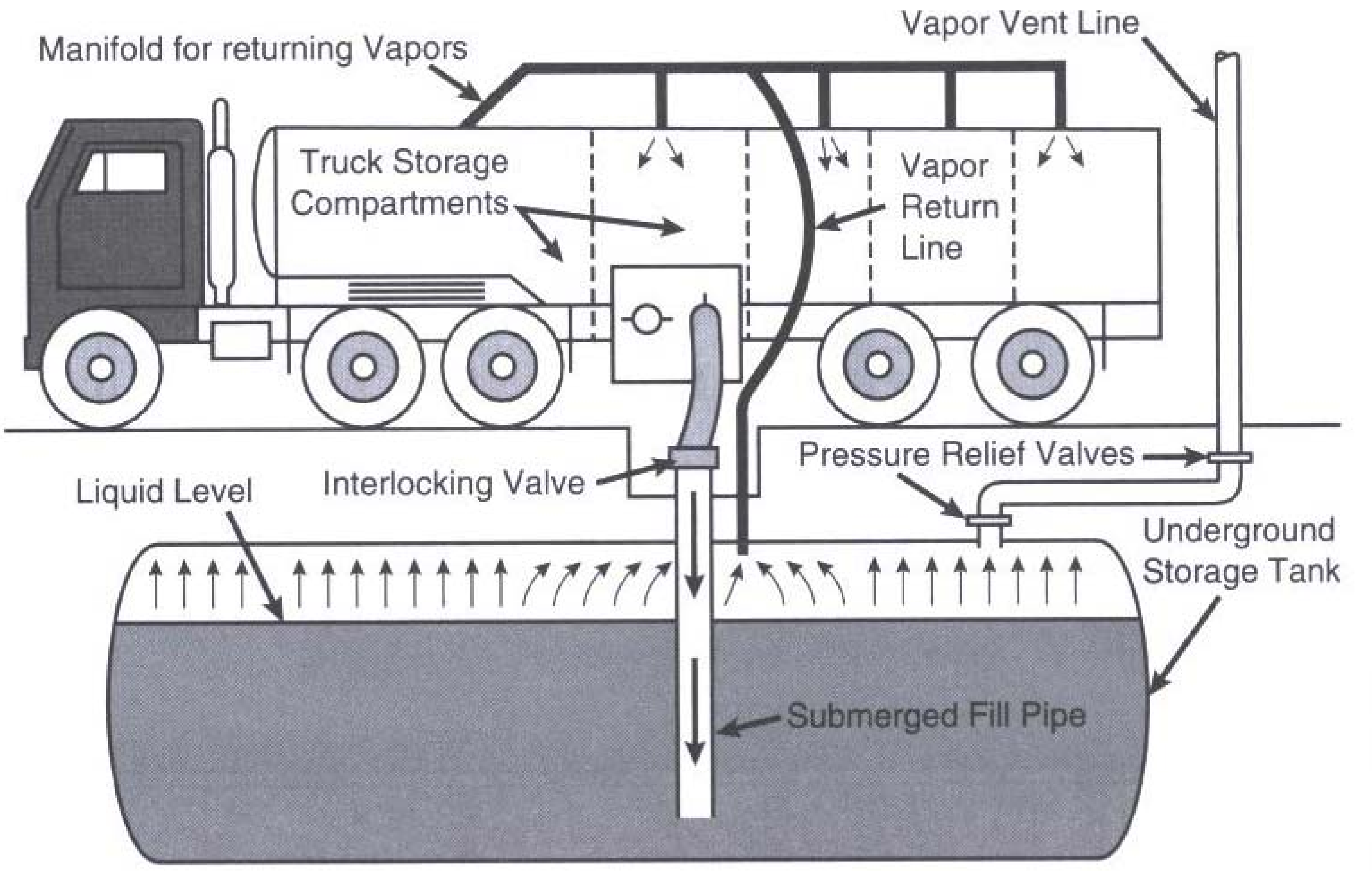


Fig. 8.3-4 Tank truck unloading into a service station underground storage tank, practicing "vapor balancing"

Loading loss (lbs/10^3 gal)

If the evaporation rate is negligible (P<0.68 psia), emission losses estimation from loading liquid (unit of pounds per 1000 gallons of liquid loaded) can be estimated (AP-42)

$$L_L = 12.46 \times SPM/T \qquad \textbf{(8-7)}$$

where
L_L : loading loss (lbs/10^3 gal) of liquid loaded (0.5~1.45)
S : saturation factor (dimensionless, **Table 8.3-9)**
P : true vapor pressure of liquid loaded (psia)
M : molecular weight of vapors (lb/lb-mole)
T : temperature of bulk liquid loaded (R)

- For mixtures, the vapor pressure of a chemical component can be by Raoult's law

$$P_a = P \times \chi_a \qquad \textbf{(8-8)}$$

where P : vapor pressure of pure substance (atm)
χ : mole fraction of component

Emission rate for Loading (g/sec)

- Loading Transport Containers
  - Emission rate *(vapor being displaced ~generation rate)*

$$G = SMVrP/(3600RT_L) \qquad \textbf{(8-9)}$$

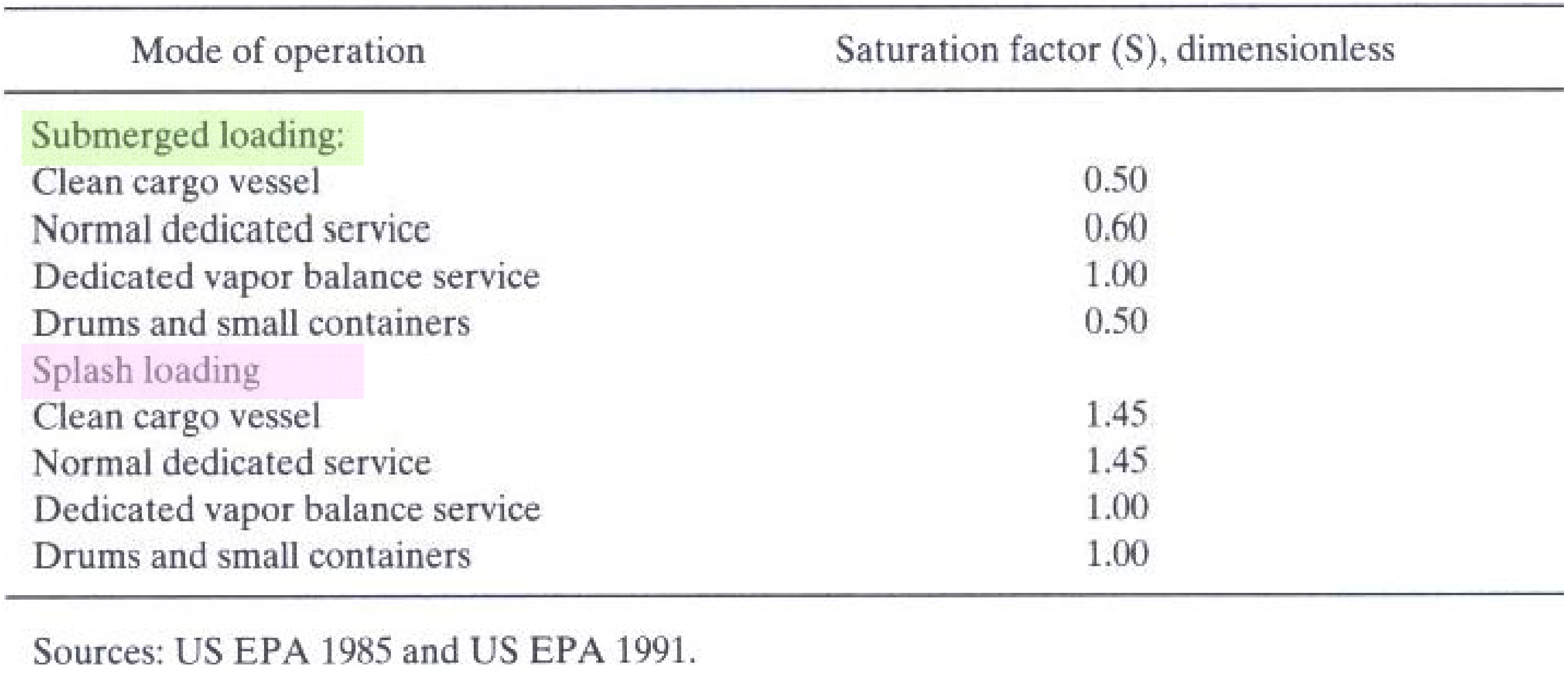
where ***G*** : vapor generation of component (g/sec)
S : saturation factor (**Table 8.3-9)**
M : molecular weight of vapors (g/g-mole)
V : volume of container (cm^3)
r : fill rate (containers/hr)
P : vapor pressure of component (atm at T_L)
R : 82.05 atm·cm^3/gmol·K
$\boldsymbol{T_L}$: liquid temperature (K)

- EPA has chosen some default factors for use when information is not available to determine ***(Table 8.3-10)***

  (Example 8.3-5)

Table 8.3-9

saturation factors (S) for loading operations



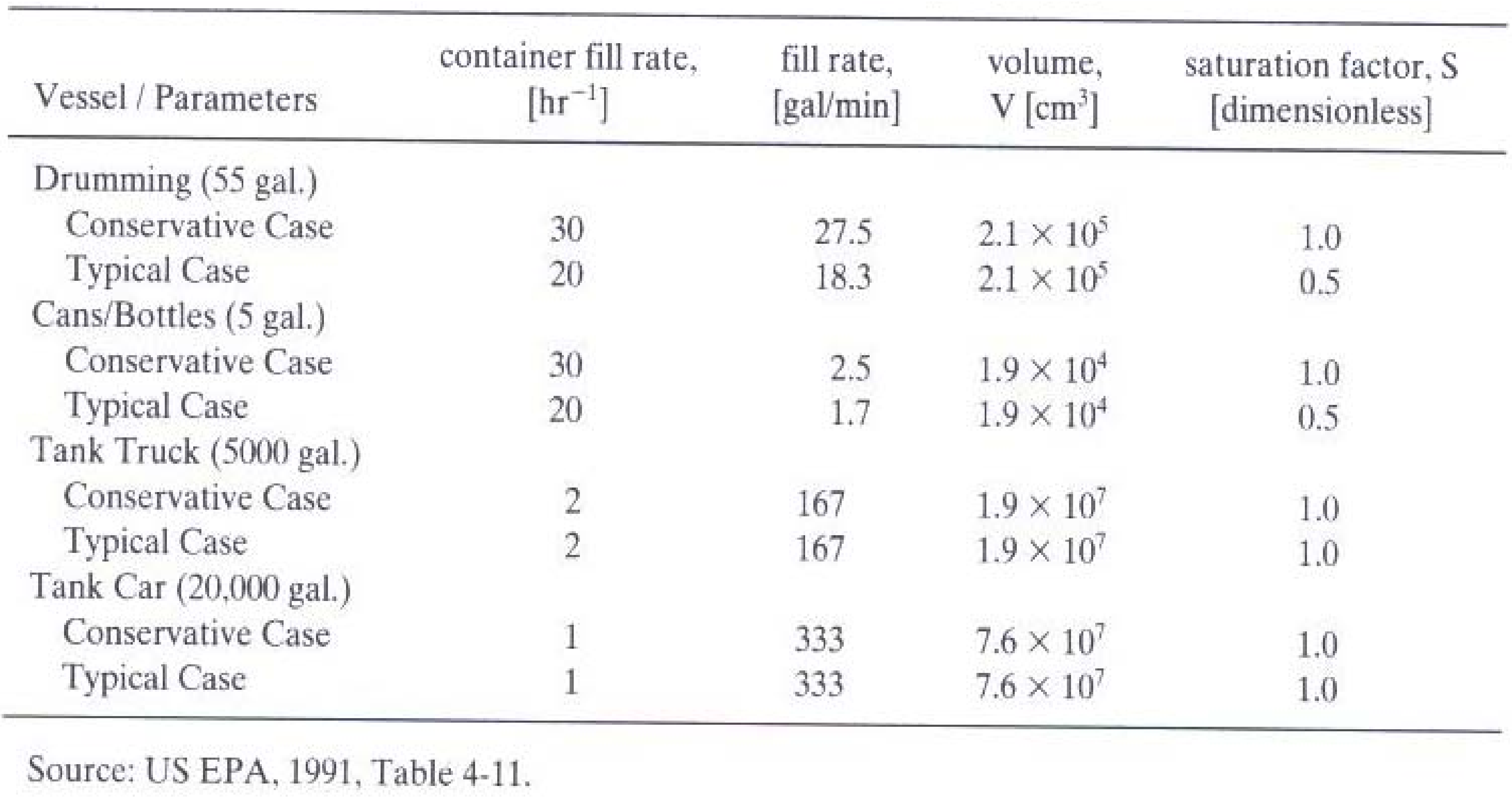
Mode of operation	Saturation factor (S), dimensionless
Submerged loading:	
Clean cargo vessel	0.50
Normal dedicated service	0.60
Dedicated vapor balance service	1.00
Drums and small containers	0.50
Splash loading	
Clean cargo vessel	1.45
Normal dedicated service	1.45
Dedicated vapor balance service	1.00
Drums and small containers	1.00

Sources: US EPA 1985 and US EPA 1991.

If complete saturation of the vapor space within a vessel is assumed, the saturation factor is equal to 1.

Table 8.3-10

Transfer operation default parameters



Vessel / Parameters	container fill rate, [hr^{-1}]	fill rate, [gal/min]	volume, V [cm^3]	saturation factor, S [dimensionless]
Drumming (55 gal.)				
Conservative Case	30	27.5	2.1×10^5	1.0
Typical Case	20	18.3	2.1×10^5	0.5
Cans/Bottles (5 gal.)				
Conservative Case	30	2.5	1.9×10^4	1.0
Typical Case	20	1.7	1.9×10^4	0.5
Tank Truck (5000 gal.)				
Conservative Case	2	167	1.9×10^7	1.0
Typical Case	2	167	1.9×10^7	1.0
Tank Car (20,000 gal.)				
Conservative Case	1	333	7.6×10^7	1.0
Typical Case	1	333	7.6×10^7	1.0

Source: US EPA, 1991, Table 4-11.

Example 8.3-5

ABC Chemical Company plans to produce and sell 50,000 pounds of n-butyl lactate (NBL) this year. All of this year product will be shipped in 55-gallon drums. ABC will produce 5,000 lb/day of NBL for 10 days, and each day's production is drummed in 30 minutes. How much of the NBL product will be emitted daily as fugitive vapors from ABC's drumming operation?

$$G = SMVrP/(3600RT_L)$$

where **G** : vapor generation of component (g/sec)

S : saturation factor **= 0.5 (Table 8.3-9)**

M : molecular weight of vapors (g/g-mole) **= 146.2**

V : volume of container (cm^3) **= 2.1×10^5 (Table 8.3-9)**

r : fill rate (drums/hr) **= 5,000 lb/day → 22 drum/hr**

P : vapor pressure of component (atm at T_L) **= 0.0005 atm**

R :gas constant **= 82.05 atm·cm^3/gmol·K**

T_L : liquid temperature (K) **= 293k**

$$G = 0.5 \times 146.2 \times 210{,}000 \times 22 \times 0.0005/(3600 \times 82.05 \times 293)$$

$$= 2.05 \times 10^{-3}\ g/sec$$

$$= 3.7 \times 10^{-3}\ kg/day$$

8.3.3.2 Evaporative Losses from Static Liquid Pools

- vapors generate from evaporation from pools of liquid that are open to air
  (e.g., open tanks, solvent dip tanks, open roller coating, cleaning, maintenance activities, spills)

- Estimate air emissions from open liquid tanks *(Hummel, 1996)*

$$G = 13.32 MPAT^{-1}(D_{ab} v_Z \Delta Z^{-1})^{0.5}$$

G : generation rate, lb/hr
M : molecular weight, lb/lb-mole
P : vapor pressure (in.Hg)
D_{ab} : diffusion coefficient, ft^2/sec of a through b(in this case air)
A : area, ft^2
v_z : air velocity, ft/min
T : temperature (K)
Δz : pool length along flow direction, ft

- Gas diffusivities of volatiles in air *(Hummel, 1996)*

$$D = 4.09 \times 10^{-5} T^{1.9} (29^{-1} + M^{-1})^{0.5} M^{-0.33} P_t^{-1}$$

8.3.3.3 Storage Tank Working and Breathing Losses

- Tanks have the potential to be major contributors to airborne emissions of volatile organic compounds from chemical facilities because of the dynamic operation of these units.

- Two major loss mechanisms from tanks
  1. *Working losses : from raising and lowering liquid level*
  2. *Standing losses : even of the tank level is static, standing losses due to every day T and P fluctuations which cause a pressure difference between the gas inside the tank and the outside air.*

- 4 Major types of storage tanks : (1) fixed-roof, (2) floating-roof, (2) variable-vapor-space, and (4) pressurized tank
  - Software for estimating emissions (1) and (2) tank is available from **EPA CHIEF** (***Appendix C and http:// www.epa.gov/ttn/chief/***)

8.3.4 Release Characterization and Documentation

Estimating releases often requires judgment, and the reliability of emission estimates based on judgment is often difficult to assesses. The uncertainty depends on (1) *how well we know the process, (2) how well we understand methods, and its data and parameters, and (3) how well the method and parameters seem to match up with those expected for the actual process.*

The factor quality rating system of the EPA is used in assessing the accuracy and representativeness of emission data. This rating system assigns a quality index of **A** through **E** and a **U** for unrated.

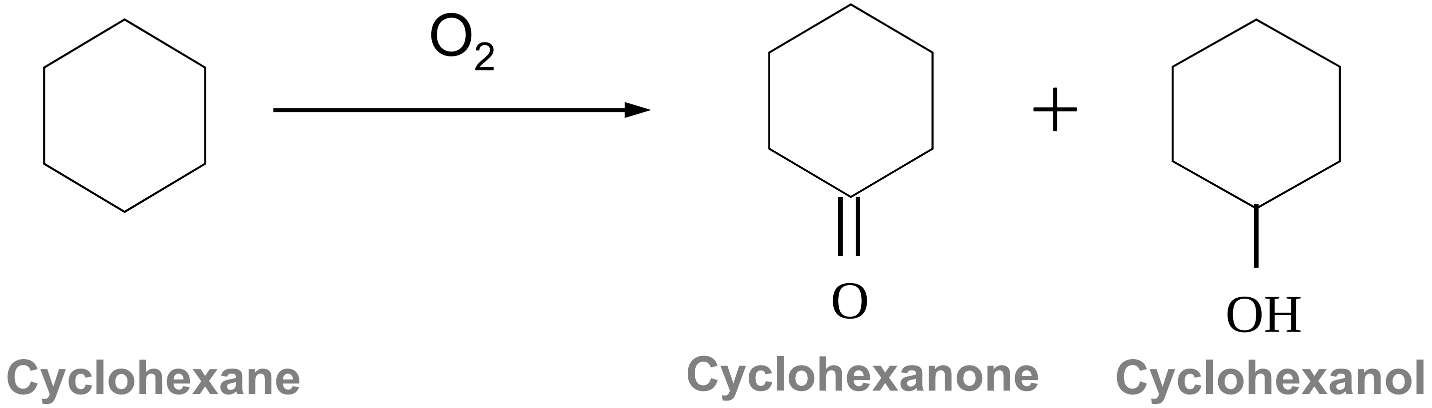
FIRE database: 650 emission factors

10 As, 22 Bs, 17Cs, 43 Ds, 558 Us

Clearly, many of the emission estimation procedures develop in this chapter provide only order of magnitude estimates of actual process emissions. After making release estimates, it can be valuable to ask whether the estimates seem realistic relative to the process flow streams.

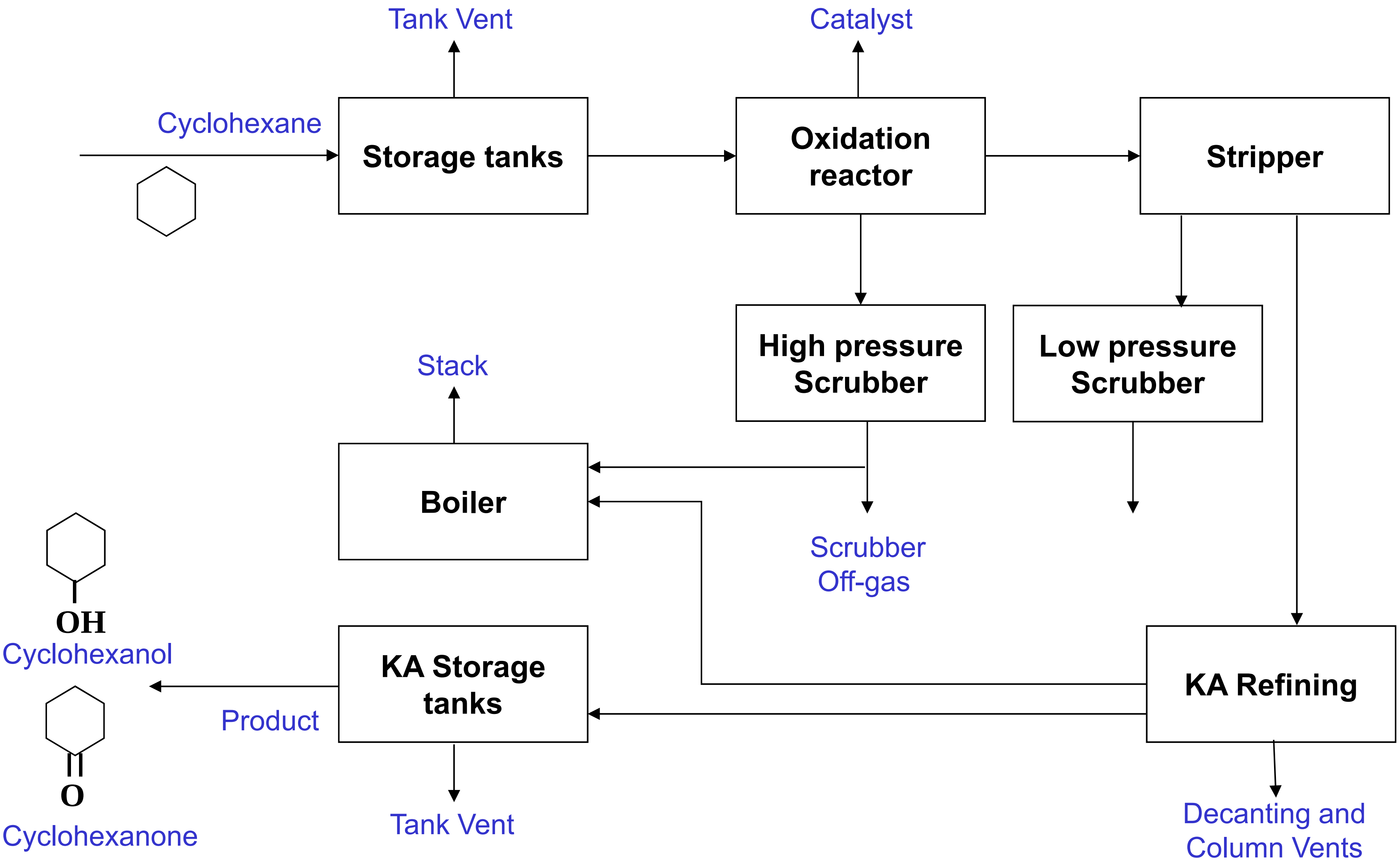
Cyclohexanone / Cyclohexanol manufacturing process

The collection of emission estimation tool will be applied to the chemical process flow sheet shown in Figure 8.3-5. This is a process in which cyclohexane is oxidized, producing cyclohexanone and cyclohexnol (a ketone/alcohol mixture). This mixture is used in the manufacture of adipic acid, which in turn is used in the production of nylon.



The first step in estimating the emissions for this flowsheet is to identify major emission sources.

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process



Tank Vent

Catalyst

Cyclohexane

Storage tanks

Oxidation reactor

Stripper

High pressure Scrubber

Low pressure Scrubber

Stack

Boiler

Scrubber Off-gas

Cyclohexanol

KA Storage tanks

KA Refining

Product

Cyclohexanone

Tank Vent

Decanting and Column Vents

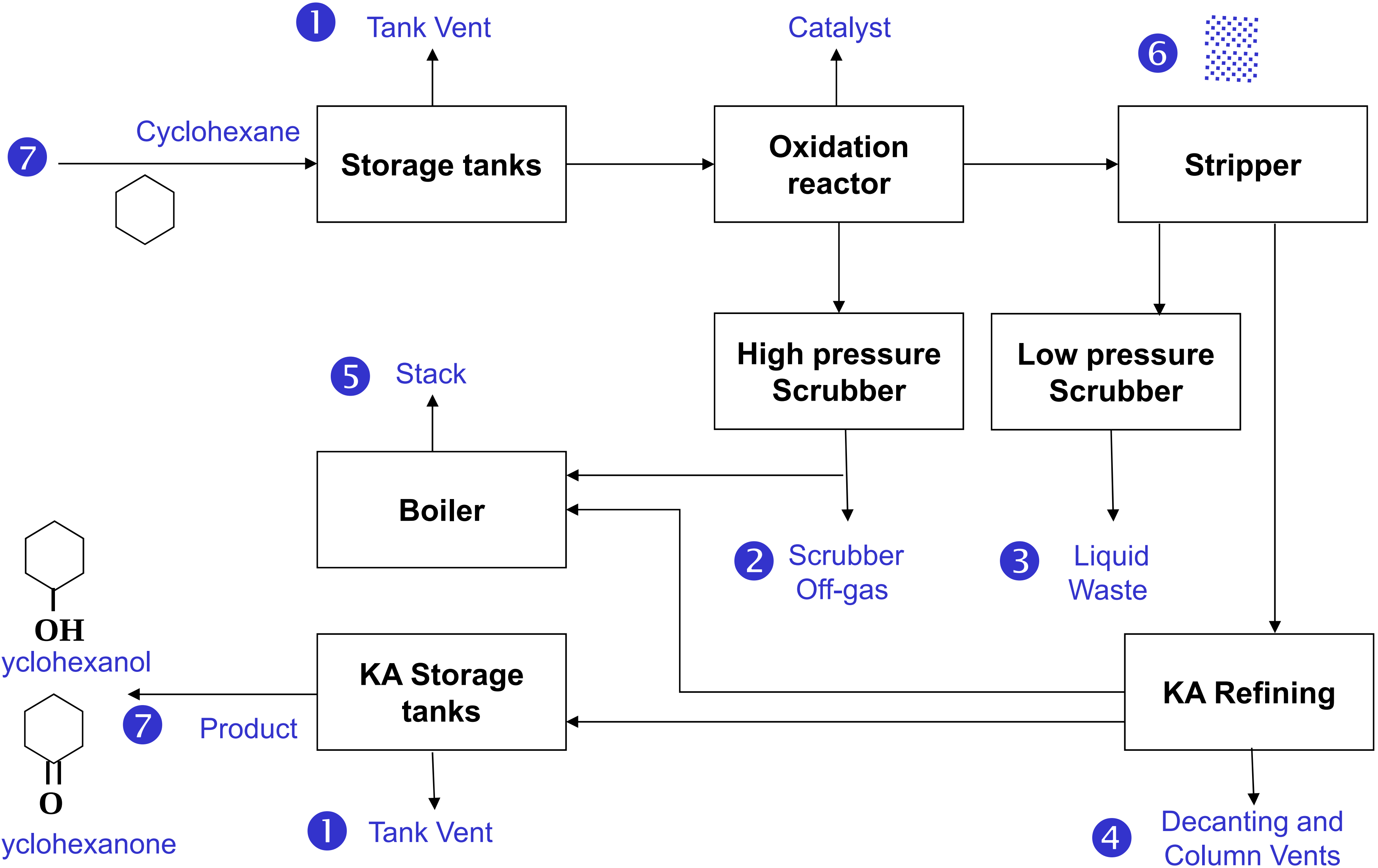
Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

Among the major source of emissions from this process are:

1. **Venting from the feed and product storage tanks**
2. **Off-gases from the scrubbers**
3. **Liquid waste from the scrubbers**
4. **Emissions from the decanting and purification columns**
5. **Emissions from the boilers**
6. **Fugitive emissions**
7. **Feed and product loading and off-loading emissions**

Each of these emissions can be calculated, at varying levels of detail, using the methods described in this chapter.

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process



① Tank Vent

Catalyst

⑥ ▨

⑦ Cyclohexane

Storage tanks

Oxidation reactor

Stripper

High pressure Scrubber

Low pressure Scrubber

⑤ Stack

Boiler

② Scrubber Off-gas

③ Liquid Waste

OH

Cyclohexanol

KA Storage tanks

KA Refining

⑦ Product

O

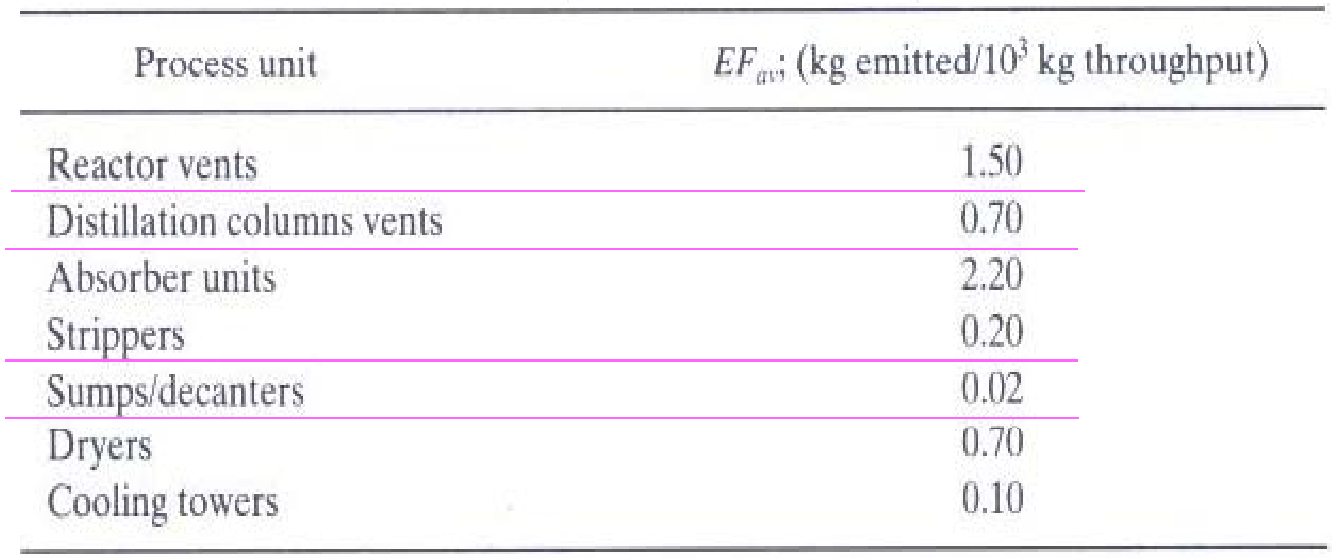
Cyclohexanone

① Tank Vent

④ Decanting and Column Vents

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

Emissions from reactors, stripper, decanter, and distillation column. Since no direct process data have been provided for these units, the emissions should be estimated from the general emission factors listed in Table 8.3-2.



Process unit	EF_{av}; (kg emitted/10^3 kg throughput)
Reactor vents	1.50
Distillation columns vents	0.70
Absorber units	2.20
Strippers	0.20
Sumps/decanters	0.02
Dryers	0.70
Cooling towers	0.10

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

For the reactor, we might assume that half of the emissions are reactants (cyclohexane), and half are products (ketone and aldehyde). For the stripper, decanter, and distillation columns, it can be assumed that all of the emissions are product. This leads to total emissions for this section of 0.8 kg/10^3 kg throughput for cyclohexane and 1.6 kg/10^3 kg throughput for the ketone and alcohol.

As a next step for emission from boiler,an estimate of energy consumption per kg product is required. Rudd (1981) provides estimates of energy consumption for a number of processes and suggest a value of 0.5 metric tons of fuel oil equivalent per metric ton (10^3 kg) of product. Assuming that #6 fuel oil with 1% sulfur is used and that no emission controls are in place leads to estimate (based on Table 8.3-5) of:

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

Emission from boilers (based on Table 8.3-5) :

SO_2 = 19 kg /10^3 L fuel oil x 0.8 kg/L x 500 kg fuel oil / 10^3 kg product

= 7.6 kg SO_2/10^3 kg product

SO_3 = 0.69 kg/10^3 L fuel oil x 0.8 kg/L x 500 kg fuel oil / 10^3 kg product

= 0.3 kg SO_3/10^3 kg product

NO_x = 8 kg/10^3 L fuel oil x 0.8 kg/L x 500 kg fuel oil / 10^3 kg product

= 3.2 kg NO_x/10^3 kg product

PM = 1.5 kg/10^3 L fuel oil x 0.8 kg/L x 500 kg fuel oil / 10^3 kg product

= 0.6 kg PM/10^3 kg product

Fugitive emissions: 0.5-1.5 kg/10^3 kg product

1.5: 1.12(1)+0.37=1.49

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

Accurately estimating fugitive emissions requires a count of valves, flanges, fittings, pumps, and other devices that are used in the process. Such counts are not generally available for preliminary process designs; however, rough estimates can be made based on experience.

Typically, fugitive emissions for chemical processes total 0.5-1.5 kg per 10^3 kg product (Berglund and Hansen, 1990). In this case, we have probably already accounted for some of the fugitive emissions through the emission factors for the reactors and distillation column; therefore an estimate of 0.5 kg per 10^3 kg product is appropriate, with the emissions evenly split between products and reactants.

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

The remaining emissions include (1) emissions from loading and off-loading emissions, (2) emissions from tanks, and (3) the off-gases and liquid wastes from the scrubbers.

The emissions from loading and off-loading (1) could be estimated using Equation 8-7. Assuming a saturation factor of 0.6 (Table 8.3-9), a vapor pressure of 4.1 mm Hg for the ketone (estimated using the methods described in Chapter 5), a molecular weight of 98, and a temperature of 530 R gives a loading loss of:

L_L = 12.46 x SPM/T

= 12.46 x 0.6 x (4.1x14.7/760) x 98 /530

= 0.1 lb/10^3 gal = 0.15kg/10^3 kg product

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

Losses from tanks (2) can be estimated using the methods described in Appendix C. Without a detailed flowsheet, exact specifications for the tank are not available.

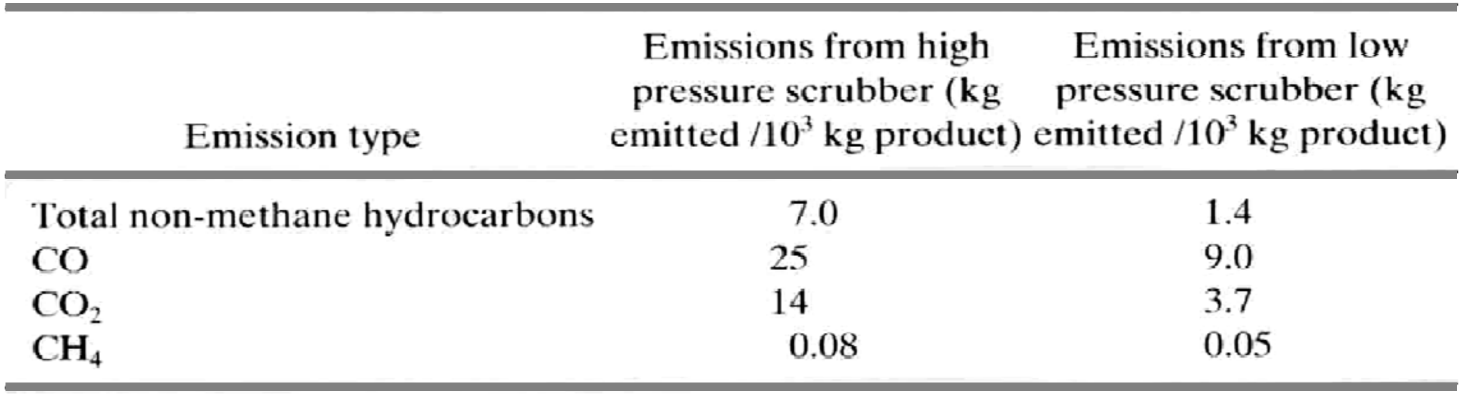
A rough estimate of tank dimensions, however, can be derived from annual production rates. If we assume a production rate of 100 million pounds per year, and that a typical tank should hold 2-3 days of production capacity, an approximate tank volume can be calculated. For this production rate, a tank 35 ft in diameter and 20 feet high with a fixed roof, is reasonable. We will also assume that, to minimize emissions, the tank is painted white, the paint is in good condition and the tank is generally kept 80% full. If the facility is located in Houston, Texas, the data and procedures described in the appendix lead to an estimate of order 0.5 kg emitted / 10^3 kg product for standing and working losses. We will assume that these are emissions of the feed material, cyclohexane.

Major sources of Emissions in Cyclohexanone/Cyclohexanol manufacturing process

The emission rate from the off-gases and liquid wastes from the scrubbers (3) should be estimated. These emissions depend strongly on the assumed efficiency of the scrubbers. If data are not available for the process of interest, it is generally a sound practice to obtain data from similar processes. For this part of the adipic acid process, AP-42 reports the gas emissions from the scrubbers shown in Table 8.3-11.

Hedley reports rates of liquid waste generation from the combined scrubbers. They suggest approximately 200 kg of organic sodium salts are generated in the scrubbers per 10^3 kg product.

Table 8.3-11 Gas phase emissions from the scrubbers in cyclohexane partial oxidation (AP-42)



Emission type	Emissions from high pressure scrubber (kg emitted /10^3 kg product)	Emissions from low pressure scrubber (kg emitted /10^3 kg product)
Total non-methane hydrocarbons	7.0	1.4
CO	25	9.0
CO_2	14	3.7
CH_4	0.08	0.05

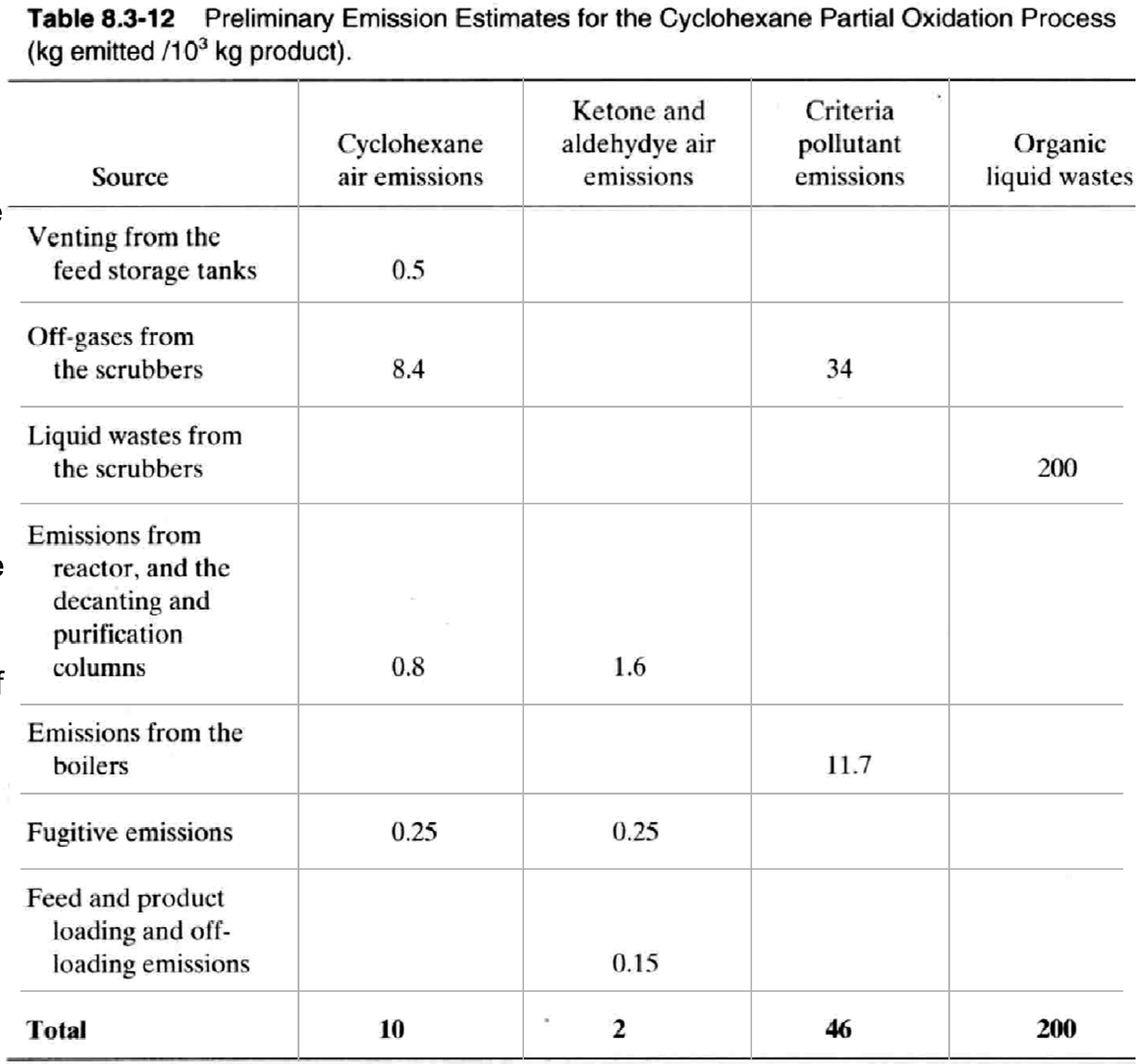


Table 8.3-12 Preliminary Emission Estimates for the Cyclohexane Partial Oxidation Process (kg emitted /10^3 kg product).

Source	Cyclohexane air emissions	Ketone and aldehydye air emissions	Criteria pollutant emissions	Organic liquid wastes
Venting from the feed storage tanks	0.5			
Off-gases from the scrubbers	8.4		34	
Liquid wastes from the scrubbers				200
Emissions from reactor, and the decanting and purification columns	0.8	1.6		
Emissions from the boilers			11.7	
Fugitive emissions	0.25	0.25		
Feed and product loading and off-loading emissions		0.15		
Total	**10**	**2**	**46**	**200**

The data summarized in Table 8.3-12 provide a reasonable starting point for estimating the environmental impacts of this chemical process.

The next section describes how these emission and order data can be converted to a set of environmental performance metrics.

8.3.5 Assessing Environmental Performance

Once preliminary estimates of material flows, energy requirements, wastes and emissions have been made for a flowsheet, the overall environmental performance of the flowsheet can be evaluated.

Two types of assessments

1. Evaluates treatability or costs of treatment of waste streams
2. Evaluate environmental performance indicators (AIChE’s CWRT, Center for Waste Reduction Technologies).

8.3.5 Assessing Environmental Performance

The environmental performance indicators are

- Energy consumed from all sources within the manufacturing or delivery process per unit of manufactured output
- Total mass of materials used directly in the product, minus the mass of the product, per unit of manufactured output
- Water consumption per unit of manufactured output
- Emission of targeted pollutants per unit of manufactured output
- Total pollutants per unit of manufactured output

Taken together, these cost and environmental performance matrix provide additional guidance on the performance of flowsheets.

8.3.5 Assessing Environmental Performance

Manufacturing 1 ton of cyclohexanol requires (Heidley, 1975)

1.64 ton of cyclohexane
0.13 ton of sodium hydroxide

and co-produce
0.38 ton of cyclohexanone (desirable)

Material intensity (excluding water)

$$= \frac{(1.64 + 0.13)\ \text{tons raw materials} - 1.38\ \text{tons products}}{(1 + 0.38)\ \text{tons products}} = 0.28$$

8.3.5 Assessing Environmental Performance

Production of Cyclohexanone and Cyclohexanol

Material use:	**0.28 lb/lb prod.**
Energy use:	**7 kBTU/lb prod.**
Water use:	**30 gal/lb prod.**
Pollutants:	**0.3 lb/lb prod.**

Are these values high? **Yes, they are.**

Compare with Table 8.3-13

pp 244-255

8.3.5 Assessing Environmental Performance

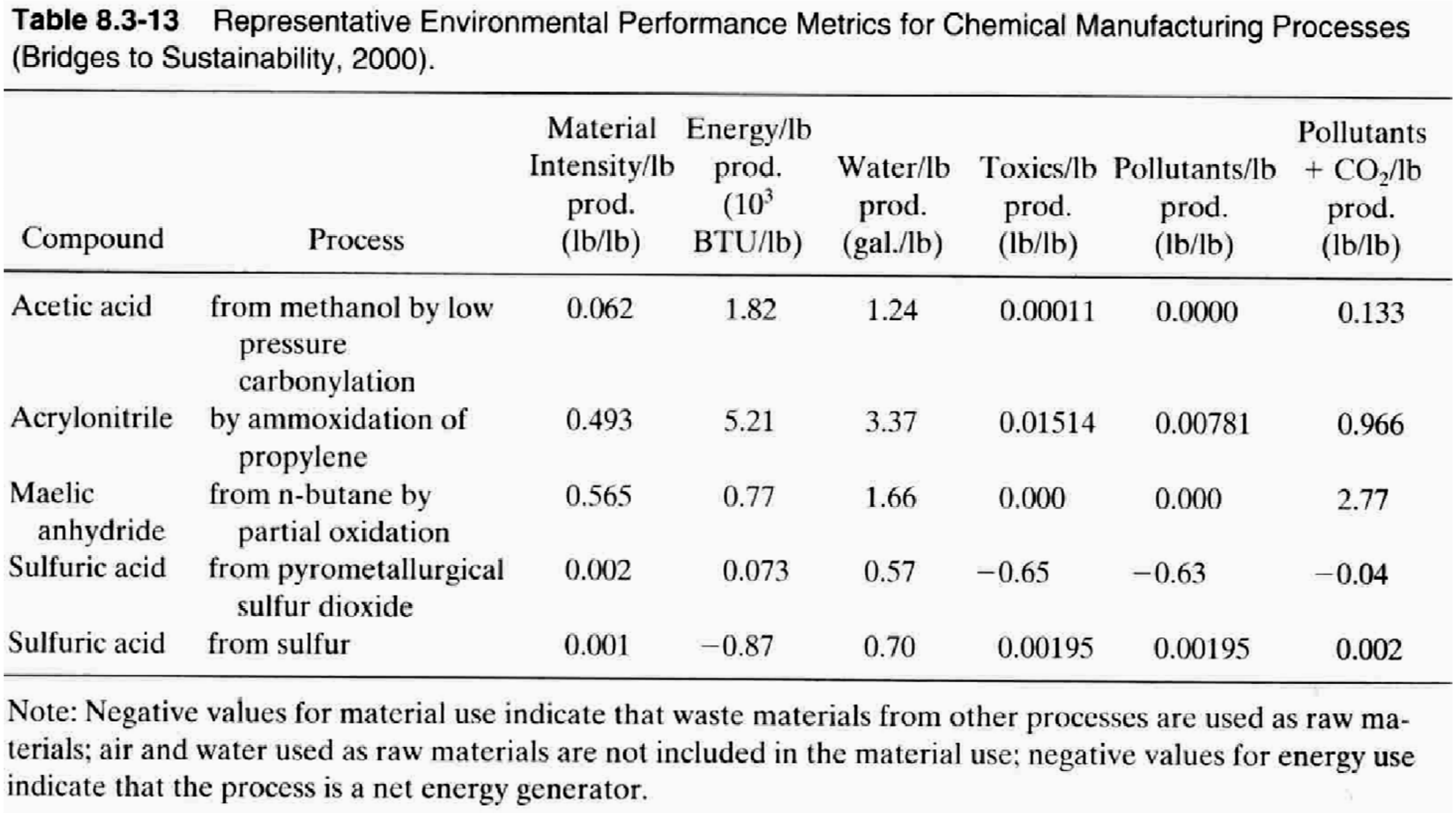


Table 8.3-13 Representative Environmental Performance Metrics for Chemical Manufacturing Processes (Bridges to Sustainability, 2000).

Compound	Process	Material Intensity/lb prod. (lb/lb)	Energy/lb prod. (10^3 BTU/lb)	Water/lb prod. (gal./lb)	Toxics/lb prod. (lb/lb)	Pollutants/lb prod. (lb/lb)	Pollutants + CO_2/lb prod. (lb/lb)
Acetic acid	from methanol by low pressure carbonylation	0.062	1.82	1.24	0.00011	0.0000	0.133
Acrylonitrile	by ammoxidation of propylene	0.493	5.21	3.37	0.01514	0.00781	0.966
Maelic anhydride	from n-butane by partial oxidation	0.565	0.77	1.66	0.000	0.000	2.77
Sulfuric acid	from pyrometallurgical sulfur dioxide	0.002	0.073	0.57	−0.65	−0.63	−0.04
Sulfuric acid	from sulfur	0.001	−0.87	0.70	0.00195	0.00195	0.002

Note: Negative values for material use indicate that waste materials from other processes are used as raw materials; air and water used as raw materials are not included in the material use; negative values for energy use indicate that the process is a net energy generator.

8.4 Tier 3 Environmental Performance Tools

- Once the basic structure of the process flowsheet is determined, detailed specifications of reactor and separator sizes, stream compositions, energy loads, and other process variables can be established
- Final environmental performance evaluation procedures
  - *methods for improving environmental performance at the level of conceptual process flowsheet ~* ***Ch. 9 and 10***
  - *methods for evaluating environmental performance at the final level ~* ***Ch. 11***

Homework #7

Problem 8-1

Due on May14, 2011