Module 2. Environmentally Conscious Design of Processes

NSF Summer Institute on Nano Mechanics and Materials: A Short Course on Nanotechnology, Biotechnology, and Green Manufacturing for Creating Sustainable Technologies

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Module 2 outline

- Principles of Green Engineering
- Green Engineering: A design approach for environmental sustainability
- Estimating environmental properties of pollutants (chapter 5)
- Estimating fate and exposure of pollutants (chapter 6)
- Estimating pollutant emissions from processes (chapter 8)
- Pollution prevention: 4 examples (chapter 9)
Principles of Green Engineering

Principles of Green Engineering:
- Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools.
- Conserve and improve natural ecosystems while protecting human health and well-being.
- Use life-cycle thinking in all engineering activities.
- Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible.
- Minimize depletion of natural resources.
- Strive to prevent waste.
- Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures.
- Create engineering solutions beyond current or dominant technologies; improve, innovate, and invent (technologies) to achieve sustainability.
- Actively engage communities and stakeholders in development of engineering solutions.

*as developed by more than 65 engineers and scientists at the Green Engineering: Defining the Principles Conference, held in Sandestin, Florida in May of 2003.

12 Principles of Green Engineering

12 Principles of Green Engineering:
- Inherent rather than circumstantial.
- Prevention rather than treatment.
- Design for separation.
- Maximize mass, energy, space, and time efficiency.
- “Output pulled” rather than “input pushed”.
- View complexity as an investment.
- Durability rather than immortality.
- Need rather than excess.
- Minimize material diversity.
- Integrate local material and energy flows.
- Design for a commercial “afterlife”.
- Renewable and readily available.

Green Engineering: A Design Approach for Environmental Sustainability

- **Molecular level to global scale**
  - Chemical structure ⇒ environmental fate properties
- **Hierarchy of design activities**
  - Early to detailed flowsheet assessment
- **Beyond the plant boundary considerations**
  - Life cycle assessment and industrial ecology
- **Integration of traditional disciplines**
  - Environmental science into engineering design
  - Total cost accounting

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2-minute discussion

Where does your research / teaching fit in this environmentally conscious design approach?

- Do you work at the molecular scale in the development of new materials?
- Does your work involve process applications?
- Are most or your efforts on the systems scale?
- How do we evaluate environmental issues at these scales?
Tools for Environmentally-Conscious Process Design and Analysis

Chemical Process Properties
- thermodynamics
- reactions
- transport

Environmental Fate Properties
- databases
- estimation

Chemical Process Models
- simulation
- waste generation and release

Environmental Fate Models
- single compartment
- multi-media

Environmental Impacts Models
- midpoint vs endpoint
- normalization
- valuation

Pollution Prevention
- mass integration
- heat integration
- energy sources

Process Optimization
- multi-objective
- mixed integer
- non-linear

Hierarchical Design

Hierarchical approach to environmentally conscious design

Process Design Stages

Environmental Assessments

Level 1. Input Information
- problem definition

Level 2. Input-Output Structure
- material selection
- reaction pathways

Levels 3 & 4.
- recycle
- separation system

Levels 5 - 8.
- energy integration
- detailed evaluation
- control
- safety

Simple (“tier 1”) toxicity potential, raw material costs

“tier 2” – material/energy intensity, emissions, costs

“tier 3” – emissions, environmental fate, risk, discounted cash flow


Allen, D.T. and Shonnard, D.R.
Computer-aided tools

- **Web Resources**
  - 24 sites with information on many aspects of green engineering

- **On-Line Databases**
  - Environmental properties, human and ecosystem toxicity, solvent substitution

- **Software**
  - Emissions from process units (air, water, and land), workplace exposure, property estimation, environmental fate modeling, prediction of toxicity, solvent design, expert system for green chemistry, flowsheet impact assessment.

Compilation in: Appendix F.

Environmental properties are needed to predict exposure
### Chemical properties for environmental decision-making (chapter 5)

**Table 5.1-1 Chemical properties needed to perform environmental risk screenings**

<table>
<thead>
<tr>
<th>Environmental Process</th>
<th>Relevant Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimates of dispersion and fate</td>
<td>Volatility, density, melting point, water solubility, octanol-water partition coefficient, soil sorption coefficient</td>
</tr>
<tr>
<td>Persistence in the environment</td>
<td>Atmospheric oxidation rate, aqueous hydrolysis rate, photolysis rate, rate of microbial degradation</td>
</tr>
<tr>
<td>Uptake by organisms</td>
<td>Volatility, lipophilicity, molecular size, degradation in organism</td>
</tr>
<tr>
<td>Human uptake</td>
<td>Transport across dermal layers, transport rates across lung membrane, degradation rates within the human body</td>
</tr>
<tr>
<td>Toxicity and other health effects</td>
<td>Dose-response relationships</td>
</tr>
</tbody>
</table>

### Environmental properties

**Table 5.2-1 Properties that influence environmental phase partitioning**

<table>
<thead>
<tr>
<th>Property</th>
<th>Definition</th>
<th>Significance in estimating environmental fate and risks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (T_m)</td>
<td>Temperature at which solid and liquid coexist at equilibrium</td>
<td>Sometimes used as a correlating parameter in estimating other properties for compounds that are solids at ambient or near-ambient conditions</td>
</tr>
<tr>
<td>Boiling point (T_b)</td>
<td>Temperature at which the vapor pressure of a compound equals atmospheric pressure; normal boiling points (temperature at which pressure equals one atmosphere) will be used in this text</td>
<td>Characterizes the partitioning between gas and liquid phases; frequently used as a correlating variable in estimating other properties</td>
</tr>
<tr>
<td>Vapor pressure (P_v)</td>
<td>Partial pressure exerted by a vapor when the vapor is in equilibrium with its liquid</td>
<td>Characterizes the partitioning between gas and liquid phases</td>
</tr>
</tbody>
</table>
### Environmental properties (cont.)

<table>
<thead>
<tr>
<th>Property</th>
<th>Definition</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Henry’s law constant (H)</strong></td>
<td>Equilibrium ratio of the concentration of a compound in the gas phase to the concentration of the compound in a dilute aqueous solution (sometimes reported as atm·m$^3$/mol; dimensionless form will be used in this text)</td>
<td>Characterizes the partitioning between gas and aqueous phases</td>
</tr>
<tr>
<td><strong>Octanol-water partition coefficient ($K_{ow}$)</strong></td>
<td>Equilibrium ratio of the concentration of a compound in octanol to the concentration of the compound in water</td>
<td>Characterizes the partitioning between hydrophilic and hydrophobic phases in the environment and the human body; frequently used as a correlating variable in estimating other properties</td>
</tr>
<tr>
<td><strong>Water solubility (S)</strong></td>
<td>Equilibrium solubility in mol/L</td>
<td>Characterizes the partitioning between hydrophilic and hydrophobic phases in the environment</td>
</tr>
<tr>
<td><strong>Soil sorption coefficient ($K_{oc}$)</strong></td>
<td>Equilibrium ratio of the mass of a compound adsorbed per unit weight of organic carbon in a soil (in µg/g organic carbon) to the concentration of the compound in a liquid phase (in µg/ml)</td>
<td>Characterizes the partitioning between solid and liquid phases in soil which in turn determines mobility in soils; frequently estimated based on octanol-water partition coefficient, and water solubility</td>
</tr>
<tr>
<td><strong>Bioconcentration factor (BCF)</strong></td>
<td>Ratio of a chemical's concentration in the tissue of an aquatic organism to its concentration in water (reported as L/kg)</td>
<td>Characterizes the magnification of concentrations through the food chain</td>
</tr>
</tbody>
</table>
Property estimation methods based on chemical structure

Assumption:

A molecule is composed of a collection of functional groups or molecular fragments and that each group or fragment contributes in a well-defined manner to the properties of the molecule.

Functional groups

- $K_{OW}$ - octanol-water partitioning
  
  Describes partitioning of organic pollutants between the water phase and octanol

  $$\log K_{ow} = 0.229 + \Sigma n_i f_i + \Sigma n_j c_j$$

  $n$ = number of functional groups of types $i$ or $j$
  $f_i$ = contribution to $\log K_{ow}$ of group $i$
  $c_j$ = correction factor for functional group $j$
Functional groups
1,1-Dichloroethylene example

the molecular structure, \( \text{CH}_2=\text{CCl}_2 \)

one \( =\text{CH}_2 \) group

one \( =\text{CH}^- \) or \( =\text{C}< \) group

two \( -\text{Cl} \) (olefinic attachment) groups

\[
\log K_{ow} = 0.229 + 0.5184 + 0.3836 + 2(0.4923) = 2.11
\]
(no correction groups)

Experimental \( \log K_{ow} = 2.13 \)

Bond types

- \( H \) - Henry’s law constant

*Describes partitioning of organic pollutants between the water phase and air in the environment*

\[
-\log H = \Sigma n_i \, h_i + \Sigma n_j \, c_j
\]

\( n \) = number of bonds of types \( i \) or \( j \)

\( h_i \) = contribution to \( H \) of bond type \( i \)

\( c_j \) = functional group correction factor
Bond types:
1-propanol example

the molecular structure,

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

*From Table 5.2-13*

7 C-H bonds, 2 C-C bonds, 1 C-O bond, and 1 O-H bond

\(-\log H = 7(-0.1197) + 2(0.1163) + 1.0855 + 3.2318 = 3.7112\)

w correction; \(-\log H = 3.7112 - 0.20 = 3.5112\)

*Table 5.2-14*

Experimental \(-\log H = 3.55\)

---

**Molecular connectivity**

- \(K_{OC}\) - Organic carbon-water partition coeff.

*Describes partitioning of organic pollutants between the water phase and natural organic matter in soils / sediments*

\[
\log K_{oc} = 0.53^1\chi + 0.62 + \Sigma n_jP_j
\]

\(^1\chi = 1^{st} \text{order molecular connectivity index}\)

\(n_j = \text{number of groups of type } j\)

\(P_j = \text{correction factor for group } j\)
Molecular connectivity
1-hexanol example

The molecular structure, see Appendix B for details

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O} - \text{H} \\
\delta & \quad \delta \\
(1) & \quad (2) \\
(1,2) & \quad (2,2) \\
(2,2) & \quad (2,2) \\
(2,2) & \quad (2,2) \\
(2,1) & \quad (1) - \text{C atom connectivity} \\
\end{align*}
\]

\[\delta_i, \delta_j\) \quad (1,2) \quad (2,2) \quad (2,2) \quad (2,2) \quad (2,2) \quad (2,1) \quad - \text{bond connectivity} \]

\[
\chi^1 = \Sigma (\delta_i \delta_j)^{0.5} \\
\chi^1 = (1/\sqrt{2}) + (1/\sqrt{4}) + (1/\sqrt{4}) + (1/\sqrt{4}) + (1/\sqrt{4}) + (1/\sqrt{2}) = 3.41
\]

\[
\log K_{oc} = 0.53 \chi^1 + 0.62 + \Sigma n_j P_j \\
\log K_{oc} = 0.53 (3.41) + 0.62 + (-1.519) = 0.91
\]

Experimental \(\log K_{oc} = 1.01\) aliphatic alcohol

Correction factors

Chemical structure provides an incomplete description of molecular interactions leading to observable properties

Correction Factors for intermolecular forces

» Electronic interactions
» Multiple hydrogen bonding
» Substituent effects
EPIWIN collection of software programs -
Properties covered:

- Properties used to estimate partitioning: boiling point, vapor pressure, octanol-water partition coefficient, bioconcentration factor, Henry’s law coefficient, soil sorption

- Properties that govern environmental fate: atmospheric lifetimes, biodegradation rates

*Downloadable Version, http://www.epa.gov/oppt/exposure/docs/episuite.htm*

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Case study 1:
Environmental partitioning case study

**Water Compartment Only**
- 1 kg Hexachlorobenzene (Hx)
- $10^5$ m$^3$ volume of water
- $10^{-3}$ kg organic carbon / m$^3$ water
- 0.1 kg fish / 100 m$^3$ water

**Human Exposure : Fish Ingestion**
- 0.5 kg of fish consumed

Dose due to ingestion?

Concentration in the Fish (mg/kg)?

*Mackay et al., “Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals”, Lewis Publishers, 1992*
Case study 1:  
Mass balance equation for Hx 118-74-1

\[ M_{Hx} = M_{Hx,W} + M_{Hx,S} + M_{Hx,F} = V_W C_W + V_W \rho_{oc} K_{oc} C_W + V_W \rho_F BCF C_W \]

Mass balance calculations for Hx 118-74-1

Concentration in Water

\[ C_W = \frac{M_{Hx}}{(V_W + V_W \rho_{oc} K_{oc} 10^{-3} + V_W \rho_F BCF 10^{-3})} = 9.92 \times 10^{-6} \approx 10^{-5} \frac{kg \ Hx}{m^2 \ Water} \]

Concentration in Fish

\[ C_F = BCF \times C_W = (5152 \frac{L}{kg \ Fish}) (10^{-5} \frac{kg \ Hx}{m^3 \ Water}) (10^{-3} \frac{m^3 \ Water}{L}) = 5.2 \times 10^{-5} \frac{kg \ Hx}{kg \ Fish} \]

Dose to Humans

\[ Dose = M_F \times C_F = (0.5 \ kg \ Fish)(5.2 \times 10^{-5} \frac{kg \ Hx}{kg \ Fish}) = 0.026 \ g \ Hx \]
### Maleic anhydride 108-31-6
#### EPIWIN (estimates) vs ChemFate (data)

<table>
<thead>
<tr>
<th>Properties</th>
<th>EPIWIN</th>
<th>ChemFate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioling Pt. (°C)</td>
<td>156.4</td>
<td>202</td>
</tr>
<tr>
<td>Melting Pt. (°C)</td>
<td>-51.6</td>
<td>52.8</td>
</tr>
<tr>
<td>Vapor Press. @25°C (mm Hg)</td>
<td>2.97</td>
<td>.25</td>
</tr>
<tr>
<td>log $K_{ow}$</td>
<td>1.62</td>
<td>-----</td>
</tr>
<tr>
<td>Water Solubility (mg/L)</td>
<td>4912</td>
<td>-----</td>
</tr>
<tr>
<td>H (atm•m^3/mole)</td>
<td>1.9x10^6</td>
<td>-----</td>
</tr>
<tr>
<td>Biodegradation half life</td>
<td>weeks</td>
<td>-----</td>
</tr>
<tr>
<td>Hydrolysis half life</td>
<td>-----</td>
<td>1 minute</td>
</tr>
<tr>
<td>Atmos. Oxidation half life (d)</td>
<td>4.71</td>
<td>0.7</td>
</tr>
<tr>
<td>log $K_{oc}$</td>
<td>0</td>
<td>-----</td>
</tr>
<tr>
<td>Bioconcentration Factor</td>
<td>0.546</td>
<td>-----</td>
</tr>
</tbody>
</table>

*No data because MA hydrolyzes in 1 minute in water*


### Benzene 71-43-2
#### EPIWIN (estimates) vs ChemFate (data)

<table>
<thead>
<tr>
<th>Properties</th>
<th>EPIWIN</th>
<th>ChemFate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioling Pt. (°C)</td>
<td>102.24</td>
<td>80.09</td>
</tr>
<tr>
<td>Melting Pt. (°C)</td>
<td>-77.92</td>
<td>5.53</td>
</tr>
<tr>
<td>Vapor Press. @25°C (mm Hg)</td>
<td>34</td>
<td>95</td>
</tr>
<tr>
<td>log $K_{ow}$</td>
<td>1.99</td>
<td>2.13</td>
</tr>
<tr>
<td>Water Solubility (mg/L)</td>
<td>2000</td>
<td>1790</td>
</tr>
<tr>
<td>H (atm•m^3/mole)</td>
<td>5.39x10^{-3}</td>
<td>5.55x10^{-3}</td>
</tr>
<tr>
<td>Biodegradation half life</td>
<td>weeks-months</td>
<td>week</td>
</tr>
<tr>
<td>Hydrolysis half life</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Atmos. Oxidation half life (d)</td>
<td>5.5</td>
<td>10</td>
</tr>
<tr>
<td>log $K_{oc}$</td>
<td>2.22</td>
<td>1.69</td>
</tr>
<tr>
<td>Bioconcentration Factor</td>
<td>0.94</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Identifying and estimating air emissions (chapter 8)

1. Identify waste release sources in process flowsheets and mechanisms for unit operations
2. Methods for estimating air emissions from processes
3. Case study - Benzene to Maleic Anhydride process evaluation

Typical waste emission sources from chemical processes

1. Waste streams from process units
2. **Major equipment** - vents on reactors, column separators, storage tanks, vacuum systems, ..
3. **Fugitive sources** - large number of small releases from pumps, valves, fittings, flanges, open pipes, ..
4. **Loading/unloading** operations
5. Vessel clean out, **residuals** in drums and tanks
6. **Secondary sources** - emissions from wastewater treatment, other waste treatment operations, on-site land applications of waste, ..
7. Spent catalyst residues, column residues and tars, sludges from tanks, columns, and wastewater treatment, …
8. **Energy consumption** - criteria air pollutants, traces of hazardous air pollutants, greenhouse gases
Distillation column emission and waste generation mechanisms

**Inert gas for safety**

![Diagram of distillation column with emissions and waste generation]

- **Feed Tank**
- **Feed** $F, x_F, x_{F,I}$
- **Distillation Column**
- **Condenser**
- **Reboiler**
- **Distillate** $D, x_D, x_{D,I}$
- **Bottoms** $B, x_B, x_{B,I}=0$
- **Vent air emissions**
- **Still**
- **Waste (sludges)**

High temperature degradation reactions

**Vent emissions of EtOH = \((dI/dt)(VP_{EtOH}/1 \text{ atm})\)**

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Distillation column emissions: Vent air emissions - $N_2$ mass balance

- **F**: Moles of feed.
- **$x_F$**: Mole fraction of ethanol in the feed.
- **$x_{F,I}$**: Mole fraction nitrogen in the feed.
- **D**: Moles of overhead product.
- **$x_D$**: Mole fraction of ethanol in the overheads product.
- **$x_{D,I}$**: Mole fraction of nitrogen in the overheads product.
- **B**: Moles of bottoms product.
- **$x_B$**: Mole fraction of ethanol in the bottoms product.
- **$x_{B,I}$**: Mole fraction of nitrogen in the bottoms product = 0

\[
\frac{dI}{dt} = F x_{F,I} - D x_{D,I} - B x_{B,I}
\]

\[
D = F \frac{x_F - x_B}{x_D - x_B}
\]

\[
x_{F,I} = 0.98 \{ \exp[x_F \ln(H_{EtOH}) + (1 - x_F)\ln(H_{H_2O})] \}^{-1}
\]

\[
x_{D,I} = 0.98 \{ \exp[x_D \ln(H_{EtOH}) + (1 - x_D)\ln(H_{H_2O})] \}^{-1}
\]

**Vapor pressure of EtOH at condenser Temp.**
Distillation column emissions: Vent air emissions - N₂ mass balance

**Figure 2a.** Inert gas mole balance in a distillation column for \( F = 1 \text{ mole/hr, } x_D = 0.99, \text{ and } x_B = 0.01. \) Positive values of \( \frac{dI}{dt} \) indicate a potential for emission to the environment for all values of feed mole fraction when \( \frac{H_2}{H_1} \geq 0.5. \) This situation occurs for the most part when the inert gas is less soluble in the more volatile component.

Wastewater generation and RCRA sludges

**Reverse Osmosis**

**Oil sludge**

**Wastewater treatment**

10 kg sludge/kg ppt RCRA waste
Liquid storage tank air emissions and waste generation mechanisms

Vertical Fixed Roof Storage Tank

- Roof Manhole
- Gauge-Hatch/ Sample Well
- Gauger’s Platform
- Spiral Stairway
- Cylindrical Shell
- Shell Manhole

Tank Bottoms Waste (sludges)

Figure 7.1-1. Typical fixed-roof tank.
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Liquid storage tank emissions and waste generation mechanisms

Domed External Roof Storage Tank

Tank Bottoms Waste (sludges)

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Mechanisms of air emissions from storage tanks

Emission Mechanisms; Fixed Roof Tank

\[ LTOTAL = LSTANDING + LWORKING \]

Vapor pressure of liquid drives emissions

\( \Delta T \)  - Weather, paint color/quality
\( \Delta P \)  - Weather
Liquid Level  - liquid throughput, volume of tank

Module 4: Storage tank comparison - TANKS 4.0 Demonstration

Toluene Storage Tank Calculation

- Toluene emissions only
- 516,600 gal/yr flowrate of toluene
- 15,228.5 gallon tank for each comparison

<table>
<thead>
<tr>
<th>Storage Tank Type</th>
<th>Vertical</th>
<th>Internal</th>
<th>Domed External</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fixed Roof</td>
<td>Floating Roof</td>
<td>Floating Roof</td>
</tr>
<tr>
<td>Annual Emissions (lb)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>White Paint</td>
<td>337.6</td>
<td>66.2</td>
<td>42.8</td>
</tr>
<tr>
<td>Grey (Medium) Paint</td>
<td>489.1</td>
<td>85.1</td>
<td>52.4</td>
</tr>
<tr>
<td>Heated (White)</td>
<td>313.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poor (Grey/Medium)</td>
<td>509.7</td>
<td>81.0</td>
<td>51.5</td>
</tr>
</tbody>
</table>
Emission factors -

\( \text{CO}_2 \) from energy consumption

Table 1.3-11. DEFAULT \( \text{CO}_2 \) EMISSION FACTORS FOR LIQUID FUELS\(^a\)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>( %_{\text{CE}} )^b</th>
<th>Density(^c) (lb/gal)</th>
<th>Emission Factor (lb/10^3 gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1 (kerosene)</td>
<td>86.25</td>
<td>6.88</td>
<td>21,500</td>
</tr>
<tr>
<td>No. 2</td>
<td>87.25</td>
<td>7.05</td>
<td>22,300</td>
</tr>
<tr>
<td>Low Sulfur No. 6</td>
<td>87.26</td>
<td>7.88</td>
<td>25,000</td>
</tr>
<tr>
<td>High Sulfur No. 6</td>
<td>85.14</td>
<td>7.88</td>
<td>24,400</td>
</tr>
</tbody>
</table>

\(^a\) Based on 99% conversion of fuel carbon content to \( \text{CO}_2 \). To convert lb/gal to gram/cm\(^2\), multiply by 0.12. To convert from lb/10^3 gal to kg/m^3, multiply by 0.12.

\(^b\) Based on an average of fuel carbon contents given in references 73-74.

\(^c\) References 73, 75.

\[ E_i (\text{lb i / yr}) = \frac{EF_{\text{av}} (\text{lb i / 10^3 gal}) \times ED (\text{Btu / yr})}{HV (\text{Btu / 10^3 gal}) \times BE} \]

AP-42, Chapter 1, section 1.3, Air CHIEF CD, [www.epa.gov/ttn/chief/airchief.htm](http://www.epa.gov/ttn/chief/airchief.htm)

---

Emission factors -

pollutants from energy consumption

Table 1.3-1. CRITERIA POLLUTANT EMISSION FACTORS FOR UNCONTROLLED FUEL OIL COMBUSTION\(^a\)

<table>
<thead>
<tr>
<th>Firing Configuration (SCC)</th>
<th>( \text{SO}_2 )^3</th>
<th>( \text{NO}_x )^4</th>
<th>( \text{CO}_2 )^5</th>
<th>Filterable PM(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{Emission Factor} \ (\text{lb} / 10^3 \text{ gal}) \times \text{FACTOR RATING} )</td>
<td>( \text{Emission Factor} \ (\text{lb} / 10^3 \text{ gal}) \times \text{FACTOR RATING} )</td>
<td>( \text{Emission Factor} \ (\text{lb} / 10^3 \text{ gal}) \times \text{FACTOR RATING} )</td>
<td>( \text{Emission Factor} \ (\text{lb} / 10^3 \text{ gal}) \times \text{FACTOR RATING} )</td>
</tr>
<tr>
<td>Utility boilers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. 1 oil fired, normal firing (1-0-1-04-01)</td>
<td>1.57 A</td>
<td>5.78 C</td>
<td>67 A</td>
<td>5 A</td>
</tr>
<tr>
<td>No. 1 oil fired, tangential firing (1-0-1-04-04)</td>
<td>1.57 A</td>
<td>5.78 C</td>
<td>42 A</td>
<td>5 A</td>
</tr>
<tr>
<td>No. 2 oil fired, normal firing (1-0-1-04-05)</td>
<td>1.57 A</td>
<td>5.78 C</td>
<td>67 A</td>
<td>5 A</td>
</tr>
<tr>
<td>No. 2 oil fired, tangential firing (1-0-1-04-06)</td>
<td>1.57 A</td>
<td>5.78 C</td>
<td>42 A</td>
<td>5 A</td>
</tr>
<tr>
<td>No. 3 oil fired, normal firing (1-0-1-05-01)</td>
<td>1.48 A</td>
<td>5.78 C</td>
<td>67 A</td>
<td>5 A</td>
</tr>
<tr>
<td>No. 3 oil fired, tangential firing (1-0-1-05-05)</td>
<td>1.48 A</td>
<td>5.78 C</td>
<td>42 A</td>
<td>5 A</td>
</tr>
</tbody>
</table>

\[ E_i (\text{lb i / yr}) = \frac{EF_{\text{av}} (\text{lb i / 10^3 gal}) \times ED (\text{Btu / yr})}{HV (\text{Btu / 10^3 gal}) \times BE} \]

AP-42, Chapter 1, section 1.3, Air CHIEF CD, [www.epa.gov/ttn/chief/airchief.htm](http://www.epa.gov/ttn/chief/airchief.htm)
Pollution Prevention Example: *Comparison of NG, oil, and coal*

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas</th>
<th>Coal</th>
<th>No.6 Fuel Oil</th>
<th>No.2 Fuel Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Heating Value (MJ/kg)</td>
<td>55</td>
<td>28</td>
<td>42.5</td>
<td>42.5</td>
</tr>
<tr>
<td>% C (wt.)</td>
<td>74.8</td>
<td>78.0</td>
<td>87.3</td>
<td>87.3</td>
</tr>
<tr>
<td>% H (wt.)</td>
<td>25.23</td>
<td>-</td>
<td>10.5</td>
<td>12.6</td>
</tr>
<tr>
<td>% S (wt.)</td>
<td>-</td>
<td>1.0</td>
<td>0.84</td>
<td>0.22</td>
</tr>
<tr>
<td>% O (wt.)</td>
<td>0.0073</td>
<td>-</td>
<td>0.64</td>
<td>0.04</td>
</tr>
<tr>
<td>% N (wt.)</td>
<td>-</td>
<td>-</td>
<td>0.28</td>
<td>0.006</td>
</tr>
<tr>
<td>% Ash (wt.)</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>CO₂ Emissions (g / MJ)</td>
<td>50</td>
<td>100</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>SO₂ Emissions (g / MJ)</td>
<td>0</td>
<td>.71</td>
<td>0.40</td>
<td>0.10</td>
</tr>
</tbody>
</table>

*Natural Gas* is inherently less polluting energy source than petroleum or coal

---

Emission Factors - *major equipment*

**Table 8.3.2 Average Emission Factors for Chemical Process Units**  
*Calculated from the US EPA L&E Database*

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>$EF_{av}$; (kg emitted/10^3 kg throughput)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Vents</td>
<td>1.50</td>
</tr>
<tr>
<td>Distillation Columns Vents</td>
<td>0.70</td>
</tr>
<tr>
<td>Absorber Units</td>
<td>2.20</td>
</tr>
<tr>
<td>Strippers</td>
<td>0.20</td>
</tr>
<tr>
<td>Sumps/Decanters</td>
<td>0.02</td>
</tr>
<tr>
<td>Dryers</td>
<td>0.70</td>
</tr>
<tr>
<td>Cooling Towers</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Emission factors -
*fugitive sources; minor equipment*

### Table 8.3.3: Average Emission Factors for Estimating Fugitive Emissions

<table>
<thead>
<tr>
<th>Source</th>
<th>Service</th>
<th>Emission Factor (kg/hr/source)</th>
<th>SCCM²</th>
<th>Refinery³</th>
<th>Gas Plant⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valves</td>
<td>Hydrocarbon gas</td>
<td>0.00597</td>
<td>0.027</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Light liquid</td>
<td>0.00403</td>
<td>0.011</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Heavy liquid</td>
<td>0.00023</td>
<td>0.0002</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Hydrogen gas</td>
<td>-</td>
<td>0.0063</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pump Seals</td>
<td>Light liquid</td>
<td>0.0199</td>
<td>0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Heavy liquid</td>
<td>0.00852</td>
<td>0.021</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>-</td>
<td>0.063</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Compressor Seals</td>
<td>Hydrocarbon gas</td>
<td>0.228</td>
<td>0.83</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Hydrogen gas</td>
<td>-</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>-</td>
<td>0.063</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pressure-relief Valves</td>
<td>Hydrocarbon gas</td>
<td>0.164</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>0.007⁵</td>
<td>0.007⁵</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>All</td>
<td>-</td>
<td>0.188</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Flanges and other</td>
<td>All</td>
<td>0.00183</td>
<td>0.00025</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td>connections</td>
<td>Open-ended lines</td>
<td>0.0017</td>
<td>0.002</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oil/water separators</td>
<td>-</td>
<td>14.600⁶</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sampling connections</td>
<td>All</td>
<td>0.915</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### Emission correlations/models -
*storage tanks and waste treatment*

**Software Tools**

**Storage tanks**
TANKS 4.0 - program from EPA - [www.epa.gov/ttn/chief/tanks.html](http://www.epa.gov/ttn/chief/tanks.html)

**Wastewater treatment**
WATER8 - on Air CHIEF CD - [www.epa.gov/ttn/chief/airchief.html](http://www.epa.gov/ttn/chief/airchief.html)
EPI Suite - Epiwin

**Treatment storage and disposal facility (TSDF) processes**
CHEMDAT8 - on Air CHIEF CD
Module 2 Overview

- Principles of Green Engineering
- Green Engineering: A design approach for environmental sustainability
- Estimating environmental properties of pollutants
- Estimating fate and exposure of pollutants
- Estimating pollutant emissions from processes
- Pollution prevention: 4 examples

Module 3 preview

- Green Chemistry principles
- Inherently green chemical reactions
- Atom economy / mass economy
- Pollution prevention for chemical reactions
- Early design evaluation of reaction pathways
- Expansion of system boundaries