Module 1. Introduction to Green Manufacturing and Environmental Issues

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 1 Outline

- Green Engineering/Green Manufacturing: Expanding the “Box” on the Analysis of Chemical Processes and Products
- Overview of Environmental Issues (chapter 1)
- Risk Concepts and Risk Assessment (ch. 4)
What is Green Engineering?

Design, commercialization and use of processes and products that are **feasible** and **economical** while minimizing:

- **Risk** to human health and the environment
- Generation of **pollution** at the source

US EPA, OPPT, Chemical Engineering Branch, Green Engineering Program
http://www.epa.gov/oppt/greenengineering

Disclaimer

- This short course provides insights on how to design **chemical** processes and products to achieve reduced environmental impacts.

- Concepts are applicable to other engineering **and science** disciplines
The “Box” Concept: at the Microscale

\[ \frac{\partial \rho_A}{\partial t} = \nabla \cdot n_A + r_A \]

Continuity Equation for Species A

The “Box” Concept: at the Mesoscale

\[ Q \]

Packed-Bed Reactor

System Boundary
The “Box” Concept: at the Macroscale

The “Box” Concept: Exchanges Within/Between Facilities
The “Box” Concept: Beyond the Plant Boundary

Life-Cycle Assessment

- Materials
- Energy
- Wastes
- Pollution Control

Objective/Outcomes of Short Course

**Objective**
- Disseminate best methods and practices in Green Engineering and Life Cycle Assessment

**Learning Outcomes**
- Learn methods to assess and improve environmental performance of processes and products
- Become knowledgeable of computer aided tools for impact assessment of processes and products
2-minute discussion

What are the most important issues for you?
- Consider this and discuss with your neighbor.
- Be prepared to discuss why.
- How does your research address environmental issues?

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Values are in quadrillion (10^{15})
BTUs (British Thermal Units)


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U.S. energy overview

U.S. industry manufacturing energy use

<table>
<thead>
<tr>
<th>SIC Code</th>
<th>10¹⁵ BTUs/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>29 Petroleum/Coal Products</td>
<td>7.32</td>
</tr>
<tr>
<td>28 Chemicals / Allied Products</td>
<td>6.06</td>
</tr>
<tr>
<td>26 Paper</td>
<td>2.75</td>
</tr>
<tr>
<td>33 Primary Metals Industries</td>
<td>2.56</td>
</tr>
<tr>
<td>20 Food / Beverages</td>
<td>1.15</td>
</tr>
<tr>
<td>32 Nonmetallic Mineral Products</td>
<td>0.94</td>
</tr>
<tr>
<td>24 Wood Products</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Numbers represent roughly the % of US annual energy consumption


Global carbon flows and fuels use

** Deforestation

Numbers are in gigatons C or gigatons C/yr.


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**CO₂ and temperature in the northern hemisphere**

**Temperature rising**

- **Warming trends**
  - The concentration of carbon dioxide in the atmosphere helps determine Earth's surface temperature.
  - Both CO₂ and temperature have risen sharply since 1950.

**What’s ahead for the planet?**

- **Not the whole story**
  - Computer models that include only natural (left) or human (right) influences on climate can’t match the planet’s observed warming.

- **A persuasive match**
  - A model that includes both natural influences and human ones like greenhouse gas emissions closely tracks the observed warming—and projects that it will continue.
Global warming and related impacts

Chemical Processing

Cause and Effect Chain

- greenhouse gas emissions (CO₂, CH₄, N₂O)
- climate change; sea level change
- human mortality or life adjustments


Global warming potential

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>τ (yrs)</th>
<th>BI (atm⁻¹ cm⁻²)</th>
<th>GWF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>120.0</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td></td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td></td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>N₂O</td>
<td></td>
<td></td>
<td>310</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>CH₂Cl₂</td>
<td>0.5</td>
<td>1604</td>
<td>9</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>CHCl₃</td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>CCl₄</td>
<td>47.0</td>
<td>1195</td>
<td>1300</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>CH₃CCl₃</td>
<td>6.1</td>
<td>1209</td>
<td>100</td>
</tr>
<tr>
<td>CFC (hard)</td>
<td></td>
<td></td>
<td></td>
<td>7100</td>
</tr>
<tr>
<td>CFC (soft)</td>
<td></td>
<td></td>
<td></td>
<td>1600</td>
</tr>
<tr>
<td>CFC-11</td>
<td>CCl₃F</td>
<td>60.0</td>
<td>2389</td>
<td>3400</td>
</tr>
<tr>
<td>CFC-12</td>
<td>CCl₂F₂</td>
<td>120.0</td>
<td>3240</td>
<td>7100</td>
</tr>
<tr>
<td>CFC-13</td>
<td>CCl₃F₃</td>
<td></td>
<td></td>
<td>13000</td>
</tr>
</tbody>
</table>

BI = infrared radiation absorbance band intensity

Appendix D in:
Possible adverse effects of global warming

- Increased average temperatures and temperature extremes
- Melting of glaciers / polar ice and sea level rise
- Increased incidence of diseases such as malaria due to warmer temperatures
- Changing climate and altered weather patterns
- Disruption of land use due to droughts
- Migration of human populations
- Decreased life expectancy in some regions of the world

Potential solutions to global warming

- Increase energy efficiency of chemical production and electricity generation (cogeneration)
- Reduce fossil fuels usage (increase gas mileage for vehicles, more insulation for homes, etc.)
- Utilize renewable energy resources to a greater extent such as biomass, solar, hydroelectric, wind, ..
- Capture and sequester CO₂ from combustion gas streams
- Create chemicals with lower global warming potential
Stratospheric ozone depletion

Chemical Processing

Cause and Effect Chain

- Ozone depleting substances: CFCs, HCFCs
- Ozone layer loss
- Increase in UV
- Human mortality or life adjustments
- Ecosystem damage

Principal ingredients for ozone loss:

UV radiation & a free radical (e.g., \( X = \text{OH}, \text{NO}, \text{Cl}, \text{Br} \))

Net: \( 2\text{O}_3 + h\nu \rightarrow 3\text{O}_2 \)

Catalytic ozone destruction

1. \( \text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2 \)
2. \( \text{O}_3 + X \rightarrow XO + \text{O}_2 \)
3. \( O + XO \rightarrow X + \text{O}_2 \)
Production trends of ozone depleting substances (Fig. 1.4-3)

Stratospheric ozone depletion (cont.)
Figure 1.4-4

- CFC-12
- CFC-11

Annual Production of Fluorocarbons Reported to A.F.E.A.S 1980-1999

τ = 120 yr

τ = tropospheric reaction half-life

Slow recovery

Faster recovery
CFC mole balance: Atmosphere response to CFC phase-out

1. Troposphere (0 - 10 km) is well-mixed
2. Annual CFC production is emitted to atmosphere (assumed)

\[
\frac{dy_{CFC}}{dt} = \frac{E_{CFC}(t)}{M_{CFC} m_{ATM}} - \frac{1}{\tau} y_{CFC}
\]

I.C. \quad t=0, \quad y_{CFC} = y_{CFC,o}

\(y_{CFC}\) = mole fraction of CFC in the troposphere
\(E_{CFC}(t)\) = emission rate of CFC (g/yr) = \(E_{CFC,o} e^{at}\) (AFEAS web site)
\(M_{CFC}\) = molecular weight of CFC (g/mole)
\(m_{ATM}\) = atmosphere content (1.5x10^{20} moles) (Wallace/Hobbs, 1977, pg6)
\(\tau\) = CFC residence time in the troposphere (yr)
\(y_{CFC,o}\) = mole fraction of CFC in 1988 (Figure 1.4-3)
Effects of chemical properties on ozone depletion (Chapter 5)

Summary of Environmental Properties/Behavior
- CFCs, HCFCs, Halons partition to atmosphere nearly 100%
- Water solubility (v. low), Sorption to natural organic matter (v. low), vapor pressure and Henry’s constant (v. high)
- Persistence in the atmosphere is v. high (v. small hydroxyl radical (•OH) rate constant)
- Reactivity increases with addition of Hydrogen to molecule, e.g. HCFCs
### Table D-2 Ozone-Depletion Potentials for Several Industrially Important Compounds.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>τ (yrs)</th>
<th>k (cm³molecules⁻¹ s⁻¹)</th>
<th>X</th>
<th>ODP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl bromide</td>
<td>CH₃Br</td>
<td>47.0</td>
<td>3.1×10⁻³⁰</td>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td>Tetrachloromethane</td>
<td>CCl₄</td>
<td>6.1</td>
<td>3.2×10⁻³⁰</td>
<td>3</td>
<td>1.08</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>CH₂CCl₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFC (hard)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>CFC (soft)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>CFC-11</td>
<td>CCl₃F</td>
<td>60.0</td>
<td>2.3×10⁻³⁰</td>
<td>3</td>
<td>1.0</td>
</tr>
<tr>
<td>CFC-12</td>
<td>CCl₂F₂</td>
<td>120.0</td>
<td>1.6×10⁻³⁰</td>
<td>2</td>
<td>1.0</td>
</tr>
<tr>
<td>CFC-13</td>
<td>CCl₂F₆</td>
<td>96.0</td>
<td>1.4×10⁻³⁰</td>
<td>3</td>
<td>1.07</td>
</tr>
<tr>
<td>CFC-113</td>
<td>CCl₂F₂CCl₂</td>
<td>90.0</td>
<td>2.0×10⁻³⁰</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>CFC-114</td>
<td>CCl₂F₂CCl₂</td>
<td>120.0</td>
<td>1.6×10⁻³⁰</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>CFC-105</td>
<td>CCl₂F₂</td>
<td>400.0</td>
<td>1.0×10⁻³⁰</td>
<td>3</td>
<td>1.4</td>
</tr>
<tr>
<td>HALON-1201</td>
<td>CHBr₂F₂</td>
<td></td>
<td></td>
<td></td>
<td>1.25</td>
</tr>
<tr>
<td>HALON-1202</td>
<td>CHBr₂F₂</td>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>HALON-1211</td>
<td>CHBr₂F₂</td>
<td></td>
<td></td>
<td></td>
<td>16.0</td>
</tr>
<tr>
<td>HALON-1301</td>
<td>CHBr₂F₂</td>
<td></td>
<td></td>
<td></td>
<td>0.14</td>
</tr>
<tr>
<td>HALON-2401</td>
<td>CHBr₂FCF₅</td>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>HALON-2402</td>
<td>CHBr₂FCF₅</td>
<td></td>
<td></td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>CF₂HCl</td>
<td>15.0</td>
<td>1.0×10⁻³⁰</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>CF₂HCl₂</td>
<td>1.7</td>
<td>2.5×10⁻³⁰</td>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>HCFC-124</td>
<td>CF₂HCl₂</td>
<td>9.6</td>
<td>1.0×10⁻³⁰</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>CF₂HCl₂</td>
<td>10.8</td>
<td>1.5×10⁻³⁰</td>
<td>2</td>
<td>0.11</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>CF₂HCl₂</td>
<td>18.1</td>
<td>1.4×10⁻³⁰</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>HCFC-225e</td>
<td>CF₂HCl₂</td>
<td></td>
<td></td>
<td></td>
<td>0.025</td>
</tr>
<tr>
<td>HCFC-225eb</td>
<td>CF₂HCl₂</td>
<td></td>
<td></td>
<td></td>
<td>0.033</td>
</tr>
</tbody>
</table>

τ is the tropospheric reaction lifetime (hydroxyl radical reaction dependent) (WMO, 1990a–1992b).

* k is the reaction rate constant with atomic oxygen at 298 K (release of chlorine in the stratosphere).

* X is the number of chlorine atoms in the molecule.

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### Smog formation and related impacts

#### Cause and Effect Chain

- **Chemical Processing**
- **NOx and volatile organic substances**
- **photochemical oxidation reactions**
- **human/ecological damage from O₃ and other oxidants**

#### Cause and Effect Chain Diagrams

- **NOx**
- **VOCs**


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Smog formation potential

Table D-4  Maximum Incremental Reactivities (MIR) for Smog Formation (O2).

<table>
<thead>
<tr>
<th>Alkanes</th>
<th>MIR</th>
<th>branched</th>
<th>MIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>0.015</td>
<td>isobutane</td>
<td>1.21</td>
</tr>
<tr>
<td>ethane</td>
<td>0.25</td>
<td>neopentane</td>
<td>0.37</td>
</tr>
<tr>
<td>propane</td>
<td>0.48</td>
<td>iso-pentane</td>
<td>1.38</td>
</tr>
<tr>
<td>n-butane</td>
<td>1.02</td>
<td>2,2-dimethylbutane</td>
<td>0.82</td>
</tr>
<tr>
<td>n-pentane</td>
<td>1.04</td>
<td>2,3-dimethylbutane</td>
<td>1.07</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.98</td>
<td>2-methylpentane</td>
<td>1.50</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.81</td>
<td>3-methylpentane</td>
<td>1.50</td>
</tr>
<tr>
<td>n-octane</td>
<td>0.60</td>
<td>2,2,3-trimethylbutane</td>
<td>1.32</td>
</tr>
<tr>
<td>n-nonane</td>
<td>0.54</td>
<td>2,3-dimethylpentane</td>
<td>1.31</td>
</tr>
<tr>
<td>n-decane</td>
<td>0.46</td>
<td>2,4-dimethylpentane</td>
<td>1.50</td>
</tr>
<tr>
<td>n-undecane</td>
<td>0.42</td>
<td>3,3-dimethylpentane</td>
<td>0.71</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>0.38</td>
<td>2-methylhexane</td>
<td>1.08</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>0.35</td>
<td>3-methylhexane</td>
<td>1.40</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>0.32</td>
<td>2,2,4-trimethylpentane</td>
<td>0.93</td>
</tr>
<tr>
<td>Average</td>
<td>0.55</td>
<td>2,3,4-trimethylpentane</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Appendix D in:  

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Acid rain / Acid deposition

Cause and Effect Chain

SO2 and NOx emission to air, Acidification rxns. & acid deposition, human/ecological damage from H+ and heavy metals

Acid rain potential

Table D-3  Acid Rain Potential for a Number of Acidifying Chemicals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>$\alpha$</th>
<th>$\omega_0$ (mol H$^+$/kg kg“i”$^{-}$)</th>
<th>ARP$_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>SO$_2$ + H$_2$O + O$_3$ → 2H$^+$ + SO$_4^{2-}$ + O$_2$</td>
<td>2</td>
<td>.064</td>
<td>31.25</td>
</tr>
<tr>
<td>NO</td>
<td>NO + O$_3$ + 1/2 H$_2$O → H$^+$ + NO$_3^-$ + 3/4 O$_2$</td>
<td>1</td>
<td>.030</td>
<td>33.33</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>NO$_2$ + 1/2 H$_2$O + 1/4 O$_2$ → H$^+$ + NO$_3^-$</td>
<td>1</td>
<td>.046</td>
<td>21.74</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>NH$_3$ + 2 O$_2$ → H$^+$ + NO$_3^-$ + H$_2$O</td>
<td>1</td>
<td>.017</td>
<td>58.82</td>
</tr>
<tr>
<td>HCl</td>
<td>HCl → H$^+$ + Cl$^-$</td>
<td>1</td>
<td>.0365</td>
<td>27.40</td>
</tr>
<tr>
<td>HF</td>
<td>HF → H$^+$ + F$^-$</td>
<td>1</td>
<td>.020</td>
<td>50.00</td>
</tr>
</tbody>
</table>

Adapted from Heijungs et al., 1992

Ecology Concepts

La Grega et al., "Hazardous Waste Management, McGraw Hill

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Ecological Impacts

La Grega et al.  "Hazardous Waste Management
McGraw Hill

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Systematic risk assessment methodology

National Academy of Sciences, 1983

1. Hazard Identification (which chemicals are important?)
2. Exposure assessment (release estimation, fate and transport, dose assessment)
3. Toxicity assessment (chemical dose - response relationships)
4. Risk Characterization (magnitude and uncertainty of risk)

Result: Quantitative risk assessment (e.g. excess cancers)

Absolute risk calculation

Carcinogenic Risk Example (inhalation route)

\[
\text{Risk}_i = \frac{(C_a \times CR \times EF \times ED)}{(BW \times AT)} \times SF
\]

- **CR**: contact rate (m³ air inhaled / day)
- **EF**: exposure frequency (days exposed / yr)
- **ED**: exposure duration (yr)
- **BW**: body weight (kg)
- **AT**: averaging time (number of days in a lifetime)

**Result**: # excess cancers per 10⁶ cases in the population; 10⁻⁴ to 10⁻⁶ acceptable

**Disadvantage**: Only a single compartment is modeled / Computationally inefficient
Highly uncertain prediction of risk
Green Engineering expands the “box” in the analysis of chemical processes and products by quantifying environmental effects.

Chemicals emitted to the environment have multiple effects ultimately leading to human health impacts.

Risk assessment is a systematic methodology to estimate human health impacts of pollutants.

Module 2 preview

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