Module 5. Practicum in Evaluation

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 5 Overview:
Practicum on evaluation

- Maleic anhydride case study again: early design – to – detailed process assessment of environmental impacts

- Pulp and paper bleaching case study: Life cycle assessment integrated into early evaluation of Green Chemistry technology.
Tools for environmentally-conscious process design and analysis

Chemical Process Properties
- thermodynamics
- reactions
- transport

Chemical Process Models
- simulation
- waste generation and release

Environmental Fate Properties
- databases
- estimation

Environmental Fate Models
- single compartment
- multi-media

Environmental Impacts Models
- midpoint vs endpoint
- normalization
- valuation

Hierarchical Design

Pollution Prevention
- mass integration
- heat integration
- energy sources

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

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.
Scope of environmental impacts

Materials
  Energy
  Chemical Processing
  Wastes (releases to air, water, and soil)
    Pollution Control
      Environmental fate processes
        Midpoints
          global warming
          ozone depletion
          smog formation
          acidification
          ecological harm
        Endpoint
          Human health and ecosystem damage

Hierarchical approach to environmentally conscious design

Process Design Stages

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

Environmental Assessments

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.
Integrated process simulation and assessment and software

HYSYS

EFRAT

SCENE

PDS

SGA

DORT

AHP

OPTIMIZER

Stream information

Environmental indices

Economic indices

Objective function

Manipulated variables

HYSYS – a commercial chemical process simulator software, EFRAT – a software for calculating environmental impacts, DORT - a software to estimate equipment costs and operating costs, AHP (Analytic Hierarchy Process) – multi-objective decision analysis, PDS – Process Diagnostic Summary Tables, SGA – Scaled Gradient Analysis

Tutorial on environmentally conscious design of chemical processes

Simultaneous Comparison of Environmental and Non-Environmental Process Criteria (SCENE)

MA production: IO assumptions

**Input / Output Information**

**Reactor**
- Benzene or n-butane
- Air

**Pollution Control**
- 99% control
- CO, CO₂, H₂O, air, MA

**Product Recovery**
- 99% MA recovery
- MA, CO, CO₂, H₂O, air

**Unreacted Benzene or n-butane**
- CO₂, H₂O, air, traces of CO, MA

**Basis:** 1 mole MA

---

SCENE
EFRAT: Chemical properties
SCENE
EFRAT Software: Chemical data

SCENE
EFRAT Software: Adding emissions
SCENE
EFRAT: Emissions summary

EFRAT: Risk Index summary
Indicators for MA production:
(EFRAT)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Benzene</th>
<th>n-butane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{FR}$ (kg/mole MA)</td>
<td>$6.83 \times 10^{-6}$</td>
<td>$3.03 \times 10^{-6}$</td>
</tr>
<tr>
<td>$I_{NG}$</td>
<td>$3.32 \times 10^{-3}$</td>
<td>$3.11 \times 10^{-3}$</td>
</tr>
<tr>
<td>$I_{NH}$</td>
<td>$4.57 \times 10^{-2}$</td>
<td>$3.58 \times 10^{-2}$</td>
</tr>
<tr>
<td>$I_{SF}$</td>
<td>$1.43 \times 10^{-1}$</td>
<td>$0.00$</td>
</tr>
<tr>
<td>$I_{OD}$</td>
<td>$1.43 \times 10^{-4}$</td>
<td>$0.00$</td>
</tr>
<tr>
<td>$I_{GW}$</td>
<td>$0.00$</td>
<td>$0.00$</td>
</tr>
<tr>
<td>$I_{SP}$</td>
<td>$2.04 \times 10^{-1}$</td>
<td>$1.20 \times 10^{-1}$</td>
</tr>
<tr>
<td>$I_{AR}$</td>
<td>$2.51 \times 10^{-5}$</td>
<td>$4.37 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

**Process Diagnostic Summary Tables: Energy input/output for nC4 process**

<table>
<thead>
<tr>
<th>Stream</th>
<th>Available temperature (In,Out)(°F)</th>
<th>Available Pressure (In,Out)(psia)</th>
<th>Energy flow (MM Btu/hr)</th>
<th>% of total energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>77</td>
<td>14.696</td>
<td>0.0000</td>
<td>0.00%</td>
</tr>
<tr>
<td>n-Butane</td>
<td>50</td>
<td>22.278</td>
<td>-0.0424</td>
<td>-0.11%</td>
</tr>
<tr>
<td>Make-up solvent</td>
<td>95</td>
<td>18.13</td>
<td>0.0004</td>
<td>0.00%</td>
</tr>
<tr>
<td>Solvent pump</td>
<td>472.87–472.96</td>
<td>1.2505–18.13</td>
<td>0.0107</td>
<td>0.03%</td>
</tr>
<tr>
<td>n-Butane vaporizer</td>
<td>50–50.004</td>
<td>22.278</td>
<td>1.0059</td>
<td>2.52%</td>
</tr>
<tr>
<td>Reactor feed heater</td>
<td>160.62–770</td>
<td>22.278</td>
<td><strong>29.8800</strong></td>
<td><strong>74.90%</strong></td>
</tr>
<tr>
<td>Reboiler</td>
<td>472.87</td>
<td>1.2505</td>
<td>5.0774</td>
<td>12.73%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td><strong>39.8908</strong></td>
</tr>
<tr>
<td>Output</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Absorber off-gas</td>
<td>120.53</td>
<td>18.275</td>
<td>2.0033</td>
<td>1.80%</td>
</tr>
<tr>
<td>Distillation off-gas</td>
<td>95.043</td>
<td>0.3897</td>
<td>0.0002</td>
<td>0.00%</td>
</tr>
<tr>
<td>Crude MA</td>
<td>95.043</td>
<td>0.3897</td>
<td>0.0368</td>
<td>0.03%</td>
</tr>
<tr>
<td>Reactor 1</td>
<td>770</td>
<td>23.6340</td>
<td>21.29%</td>
<td></td>
</tr>
<tr>
<td>Reactor 2</td>
<td>770</td>
<td>23.6340</td>
<td>21.29%</td>
<td></td>
</tr>
<tr>
<td>Reactor 3</td>
<td>770</td>
<td>23.6340</td>
<td>21.29%</td>
<td></td>
</tr>
<tr>
<td>Reactor off-gas cooler</td>
<td>770–230</td>
<td>18.943</td>
<td><strong>26.8940</strong></td>
<td><strong>24.23%</strong></td>
</tr>
<tr>
<td>Solvent subcooler</td>
<td>234.95–95</td>
<td>18.13</td>
<td>7.1588</td>
<td>6.45%</td>
</tr>
<tr>
<td>Condenser</td>
<td>95.043</td>
<td>0.3897</td>
<td>4.0202</td>
<td>3.62%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td><strong>111.0153</strong></td>
</tr>
</tbody>
</table>

**Process Diagnostic Summary Tables: Manufacturing profit and loss, nC4**

<table>
<thead>
<tr>
<th>Name</th>
<th>Total ($/yr)</th>
<th>% of total cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Revenue</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>21,258,236</td>
<td>100.00%</td>
</tr>
<tr>
<td><strong>Total Sales Revenue</strong></td>
<td>21,258,836</td>
<td>100.00%</td>
</tr>
<tr>
<td><strong>Manufacturing Expenses</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Raw Materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane cost</td>
<td><strong>4,760,866</strong></td>
<td><strong>55.80%</strong></td>
</tr>
<tr>
<td>Make-up solvent</td>
<td>81,343</td>
<td>0.95%</td>
</tr>
<tr>
<td><strong>Utilities</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling water (tower)</td>
<td>159,913</td>
<td>1.87%</td>
</tr>
<tr>
<td>Electricity (on site)</td>
<td>679,014</td>
<td>7.96%</td>
</tr>
<tr>
<td>Steam (50 psig)</td>
<td>58,014</td>
<td>0.68%</td>
</tr>
<tr>
<td>Steam (600 psig)</td>
<td>580,303</td>
<td>6.80%</td>
</tr>
<tr>
<td>Natural gas</td>
<td><strong>2,212,796</strong></td>
<td><strong>25.93%</strong></td>
</tr>
<tr>
<td><strong>Total Manufacturing Expenses</strong></td>
<td>8,532,249</td>
<td>100.00%</td>
</tr>
</tbody>
</table>
Process Diagnostic Summary Tables:
Environmental impacts, nC4

Normalizations

\[ I^k_N = \frac{I^k}{I^k_N} \]

Process Index

National Index

<table>
<thead>
<tr>
<th>Chemical</th>
<th>(I_{FT})</th>
<th>(I_{NG})</th>
<th>(I_{DG})</th>
<th>(I_{GOG})</th>
<th>(I_{OD})</th>
<th>(I_{CD})</th>
<th>(I_{CDG})</th>
<th>(I_{SC})</th>
<th>(I_{SR})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur dioxide</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>1.49E+01</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>1.35E+02</td>
</tr>
<tr>
<td>TOC</td>
<td>1.36E-02</td>
<td>1.49E-02</td>
<td>6.62E+01</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>4.11E+03</td>
<td>4.24E+02</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>4.36E+02</td>
<td>0.00E+00</td>
<td>8.91E+01</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>6.09E+07</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>1.90E+01</td>
<td>0.00E+00</td>
<td>1.65E+07</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>2.33E+05</td>
<td>2.03E+03</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>7.70E+02</td>
<td>0.00E+00</td>
<td>3.01E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>2.56E+02</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>Maleic Anhydride</td>
<td>7.01E+02</td>
<td>1.00E+02</td>
<td>1.65E+07</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>3.49E+04</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>n-Butane</td>
<td>6.98E-02</td>
<td>0.00E+00</td>
<td>2.38E+05</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>6.97E+04</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>2.10E+01</td>
<td>0.00E+00</td>
<td>2.89E+03</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>4.09E+06</td>
<td>0.00E+00</td>
<td>7.16E+04</td>
</tr>
<tr>
<td>Totals</td>
<td>1.02E+03</td>
<td>7.27E+05</td>
<td>1.67E+07</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>6.54E+07</td>
<td>2.46E+03</td>
<td>7.17E+04</td>
</tr>
</tbody>
</table>

Contribution to \(I_{PC}\) 1.55% 0.34% 86.63% 0.00% 0.00% 0.00% 4.85% 0.14% 6.50%

Source: Eco-Indicator 95 framework for life cycle assessment, Pre Consultants, http://www.pre.nl

Flowsheet for MA production from n-C4: with heat integration.
Optimization using the Genetic Algorithm


Flowsheet Optimization: Genetic Algorithm

- Begin
- Population Initialization
- Fitness Evaluation
- Selection
- Crossover
- Mutation
- Convergent?
  - No
  - Yes: Stop
- Generations, 100
- Population Size, 100
- Mutation Probability, 0.04

Optimization Results: n-C4 process

AHP Ranking is Objective Function

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Unit</th>
<th>Range</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflux ratio</td>
<td>unitless</td>
<td>0.8~1.3</td>
<td>1.27</td>
</tr>
<tr>
<td>Reactor inlet tempera</td>
<td>°C</td>
<td>390~410</td>
<td>399.55</td>
</tr>
<tr>
<td>Reactor inlet pressure</td>
<td>kPa</td>
<td>153.8~173.8</td>
<td>153.80</td>
</tr>
<tr>
<td>Recycle solvent flow rate</td>
<td>kgmol/hr</td>
<td>170~230</td>
<td>230.00</td>
</tr>
<tr>
<td>Feed ratio of air to n-butane</td>
<td>unitless</td>
<td>60~70</td>
<td>62.30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Indices</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{FT}$</td>
<td>kg/yr</td>
<td>7.995E+02</td>
</tr>
<tr>
<td>$I_{NG}$</td>
<td>kg/yr</td>
<td>6.601E+04</td>
</tr>
<tr>
<td>$I_{NH}$</td>
<td>kg/yr</td>
<td>1.594E+07</td>
</tr>
<tr>
<td>$NPV$</td>
<td>MMS$</td>
<td>5.137</td>
</tr>
<tr>
<td>$I_{IFC}$</td>
<td>unitless</td>
<td>5.380E-04</td>
</tr>
</tbody>
</table>
Continuous improvement of design performance

Comparison: Early vs optimum design

- Early design screening economic and environmental indicators: How accurate are they in predicting final design performance?

**Economics:**

- n-butane: Early: 0.0207 $/mole of MA, Detailed: $5.14 MM (NPV)
- Benzene: Early: 0.0312 $/mole of MA, Detailed: $3.44MM (NPV)

**Environmental Impacts:**

- (I_PC) n-butane: Early: 2.98x10^{-4}, Detailed: 5.38x10^{-4}
- Benzene: Early: 7.93x10^{-2}, Detailed: 9.24x10^{-2}
Conclusions from MA case study

- A systematic and hierarchical approach for EC-D of chemical processes is shown.
- The EC-D approach is applied to a case study design for MA production from either benzene or n-butane.
- A number of computer-aided tools are available to facilitate EC-D.
- This approach yields a continuous improvement in both economic and environmental performance through the designs process.
- Early design assessment methods are validated using detailed design and optimization results.

Bleaching process 2

Raw Materials Needed:
- 2 x 0.1 tons ClO₂/ ton pulp
- 2 x 0.035 tons NaOH/ ton pulp

- Elemental chlorine free (ECF)

Unbeached pulp
- 85% cellulose
- 10% hemicellulose
- 5% lignin
- 9:1 water:pulp
  (1 kg pulp / L solution)

Chlorination, 70°C → ClO₂ → NaOH Wash, 50°C → Brightening, 70°C → NaOH Wash, 50°C → Brightening, 70°C → Beached pulp

Chlorinated organics
- 0.5 kg / ton pulp
- (less Persistent Bioaccumulative & Toxic)
TAML™ activators

- “tetraamido-macrocyclic ligand” activators

\[
\begin{align*}
 & \text{H}_2\text{O}_2 \\
 & \text{TAML}^\text{™} \\
 & \text{H}_2\text{O} \\
 & 2 \cdot \text{OH} \\
 & \text{Hydroxyl radical} \\
 & \text{(a natural oxidant that removes lignin)}
\end{align*}
\]

T.J. Collins, 1999 Presidential Green Chemistry Challenge Award
“TAML™ Oxidant Activators: General activation of hydrogen peroxide for green oxidation processes”

Michigan Technological University

Bleaching process 3

3 x 0.4 tons H\textsubscript{2}O\textsubscript{2} / ton pulp

- Total chlorine free – almost! (TCF)

[Diagram of bleaching process]

- Unbeached pulp
  - 85% cellulose
  - 10% hemicellulose
  - 5% lignin
  - 9:1 water:pulp
  - (1 kg pulp / L solution)

- Peroxidation, 50°C
- Peroxidation, 50°C
- Peroxidation, 50°C
- ClO\textsubscript{2}
- Brightening, 70°C

- Chlorinated organics
  - 0.0 kg / ton pulp
  - (less Persistent Bioaccumulative & Toxic)

- Beached pulp
  - 100% cellulose

50 g / ton pulp

Michigan Technological University
Energy analysis:
Expansion of system boundaries

ClO₂ bleaching

Material flow chain energy impacts

Life cycle energy analysis of pulp bleaching

- Out-of-process analysis (TAML™ process comparison)

A more complete energy efficiency analysis of the TAML™ peroxide bleaching processes must include the effects of producing and delivering the bleaching agents to the process.

There are differences in the amount of energy required for the manufacture of peroxide and of chlorine dioxide, and the differing amounts of each agent needed for bleaching will further differentiate these processes.

Functional Unit: 3 peroxide processes are equal to 2 ClO₂ / NaOH processes.
Life cycle energy analysis of pulp bleaching

<table>
<thead>
<tr>
<th></th>
<th>Energy in original units</th>
<th>Energy (Btu / ton ClO₂ or NaOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO₂ Bleaching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mining NaCl</td>
<td>1.3 MJ/kg NaCl</td>
<td>9.69x10⁷ Btu / ton ClO₂</td>
</tr>
<tr>
<td>Electrolysis of NaCl to NaClO₃</td>
<td>17.1 kWh/kg NaClO₃</td>
<td>8.35x10⁷ Btu / ton ClO₂</td>
</tr>
<tr>
<td>HCl production</td>
<td>2.5 MJ/kg HCl</td>
<td>2.32x10⁷ Btu / ton ClO₂</td>
</tr>
<tr>
<td>HCl production electricity</td>
<td>0.043 kWh/kg HCl</td>
<td>1.44x10⁷ Btu / ton ClO₂</td>
</tr>
<tr>
<td>Total from ClO₂</td>
<td></td>
<td>8.69x10⁷ Btu /ton ClO₂</td>
</tr>
<tr>
<td>NaOH production</td>
<td>21.3 MJ/kg NaOH</td>
<td>1.83x10⁷ Btu /ton NaOH</td>
</tr>
<tr>
<td>Total ClO₂ Bleaching</td>
<td></td>
<td>(1.87x10⁷ Btu/ton pulp)</td>
</tr>
</tbody>
</table>

| H₂O₂ / TAML Bleaching    |                          |                                  |
| H₂O₂ Production          |                          | 9.60x10⁶ Btu/ton H₂O₂            |
| TAML Production          |                          | 1.0x10⁸ Btu/ton TAML™            |
| Total H₂O₂ / TAML Bleaching |                          | 1.15 x 10⁷ Btu/ton pulp         |

Example Calculation: The energy required to produce one ton of ClO₂ is therefore

\[(0.867 \text{ kg NaCl / kg ClO}_2) \times (1.3 \text{ MJ / kg NaCl}) \times (2,000/2.205 \text{ kg/ton}) \times (947.8 \text{ Btu/MJ}) + (24,478 \text{ kWh / ton of ClO}_2) \times (3.411.8 \text{ Btu/kWh}) + (1.08 \text{ tons HCl/ton ClO}_2) \times (2.5 \text{ MJ/kg HCl}) \times (2,000/2.205 \text{ kg/ton}) \times (947.8 \text{ Btu/MJ}) + (1.08 \text{ tons HCl/ton ClO}_2) \times (0.043 \text{ kWh/kg HCl}) \times (2,000/2.205 \text{ kg/ton}) \times (3.411.8 \text{ Btu/kWh}) = 9.69x10⁷ + 8.35x10⁷ + 2.32x10⁶ + 1.44x10⁵ = 8.69x10⁷ \text{ Btu/ton ClO}_2.\]

Life cycle energy data from SimaPro6.0

Comparison of impacts for both bleaching processes

The net energy change from producing the chemicals for substituting H₂O₂ bleaching for ClO₂ bleaching is

\[1.15 \times 10^7 - 1.87 \times 10^7 \text{ Btu / ton pulp} = - 8.2 \times 10^6 \text{ Btu / ton pulp.}\]

This yields a total decrease in energy consumption for the TAML™ H₂O₂ bleaching process of - 8.2 x 10⁶ - 1.4 x 10⁶ = - 9.6 x 10⁶ Btu / ton pulp
Life cycle energy analysis of pulp bleaching

- Comparing energy savings over the life cycle with Pulp and Paper industry total.

Energy Decrease Percentage for Pulp and Paper Industry =

\[
0.5 \times \frac{9.6}{39.394} \times 100 = 12.2\%
\]

Compare to 1.8% energy decrease for pulp and paper industry when just the in-process energy changes are considered. This case study demonstrates the importance of considering life cycle effects at the early stage of product/process design. This conclusion is equally valid for Nanotechnology innovations.

Module 5 Review: Practicum on evaluation

- Maleic anhydride case study again: early design – to – detailed process assessment of environmental impacts

- Pulp and paper bleaching case study: Life cycle assessment integrated into early evaluation of Green Chemistry technology.
Module 6 Preview:
Life Cycle Assessment

- Introduction to life cycle assessment
- Goal and scope definition
- Life cycle inventory.
- Life cycle impact assessment
- A simple LCA of two light bulb systems
- An industrial application from BASF