The Production of Renewable Chemicals based on Sustainable Life Cycle Inventories

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Office of Research and Development, ORD
National Risk Management Research Laboratory, NRMRL
Sustainable Technology Division, STD

Some research areas:
Life Cycle Assessment, Impact Assessment, and Sustainable Chemistry

https://www3.epa.gov/

https://epa.maps.arcgis.com/apps/OnePane/basicviewer/index.html?appid=ef56449ae4f94eb1981a2df781704b70


http://savecincinnati.com/images/cincinnati%20skyline.jpg

Agenda

- Sustainability and Chemical Processes
- Sustainability Indicators
- GREENSCOPE Evaluation Tool
- GREENSCOPE Tool Demonstration and Case Study
- Sustainable Supply Chains and Life Cycles
- Challenges, Needs, and Opportunities to Advance Sustainability
- Student Opportunities at the EPA
Sustainability and Chemical Processes
Sustainable Development

• This concept was placed in 1987
• “Our common future” report from the World Commission on Environment and Development (WCED):
  “Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”
• This is the most widely accepted definition of sustainable development across the world
Sustainability for Chemical Processes

• Guidelines to achieve quality of life improvements
  – without affecting the availability of ecological goods & services

• Assess and address and environmental, social, and economic aspects affected by industry
  – identify which system components are affected
  – localize process and product aspects which generate them
  – redesign relevant processes and products & demonstrate system improvements

• Minimize or eliminate the environmental impacts and maximize the social/economic benefits
Support decision-makers to determine whether a system is becoming more or less sustainable
  – Are we doing relatively good / bad?
• What benchmarks to use?
• How close are we to achieve absolute targets?
Changes to improve sustainability at early design stages will have greater influence on the sustainability of the process during operation.
Sustainability Assessment
Chemical/Energy Process Indicators

• Triple dimensions of sustainable development
  – Environment, Society, Economy
  – Corporate level indicators
  – Assessment at corporate level

• Four areas for promoting & informing sustainability
  – Environmental, Efficiency, Economics, Energy (4E’s)
  – Decision-making at process design level
  – Taxonomy of chemical process indicators for use in process design
The GREENSCOPE Tool and Indicators

- Clear, practical, and user-friendly approach
- Monitor & predict sustainability at any process design stage
- Capable of calculating 139+ different indicators
- User can choose which indicators to calculate
- User can redefine absolute limits to fit circumstances
GREENSCOPE Sustainability Framework

• Identification and selection of two reference states for each sustainability indicator:
  – Best target: 100% of sustainability
  – Worst-case: 0% of sustainability

• Two scenarios for normalizing the indicators on a realistic measurement scale

• Dimensionless scale for evaluating a current process or tracking modifications/designs of a new (part of a) process

\[
\% \text{ Sustainability Score} = \left( \frac{\text{Actual-Worst}}{\text{Best-Worst}} \right) \times 100\%
\]
# GREENSCOPE Indicators

<table>
<thead>
<tr>
<th>Environmental (66)</th>
<th>Efficiency (26)</th>
<th>Economic (33)</th>
<th>Energy (14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specifications of process input material (e.g., hazardous)</td>
<td>Quantities of inputs required/product or a specific process task (e.g., separation)</td>
<td>A sustainable economic outcome must be achieved</td>
<td>Different thermodynamic properties used to obtain energetic sustainability scores</td>
</tr>
<tr>
<td>Operating conditions and process operation failures (health and safety hazards)</td>
<td>Mass transfer operations, energy demand, equipment size, costs, raw materials, releases</td>
<td>Based on profitability criteria for projects (process, operating unit), may or may not account for the time value of money</td>
<td>Energy (caloric); exergy (available); emergy (embodied)</td>
</tr>
<tr>
<td>Impact of components utilized in the system</td>
<td>Connect input/output with product, intermediate or operation unit</td>
<td>Some cost criteria Indicators: capital &amp; manufacturing costs; Input costs: raw material cost; Output costs: waste treatment costs</td>
<td>Zero energy consumption per unit of product trend can be best target</td>
</tr>
<tr>
<td>Potential impact of releases</td>
<td>The reference states are defined as mass fractions $0 \leq x \leq 1$</td>
<td></td>
<td>Most of the worst cases depend on the particular process or process equipment</td>
</tr>
</tbody>
</table>
**GREENSCOPE Indicators: Example**

### Specific hazardous raw materials input

\[
m_{\text{haz. mat. spec.}} = \frac{m_{\text{haz. mat.}}}{\text{Mass of product}}
\]

\[
m_{\text{haz. mat. spec.}} = \frac{\sum_{i=1}^{n} m_{\text{haz. mat.},i}}{m_{\text{product}}}
\]

#### Global warming potential

\[
\text{GWP} = \frac{\text{Total mass of CO2 equivalent produced}}{\text{Total mass of product}}
\]

\[
\text{GWP} = \frac{\sum_{i=1}^{n} m_{i,\text{out}} \times \text{PF}_{\text{CO2},i}}{m_{\text{product}}}
\]

### Sustainability value

<table>
<thead>
<tr>
<th>Sustainability value</th>
<th>Best, 100%</th>
<th>Worst, 0%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>all inputs are hazardous</td>
</tr>
</tbody>
</table>

- \( m_{\text{product}} \): mass flow of product \( i \), kg
- \( m_{\text{haz. mat.},i} \): mass flow rate of the hazardous component \( i \), kg
- \( m_{i,\text{out}} \): output mass flow rate of the component \( i \), kg
- \( \text{PF}_{\text{CO2},i} \): potency factor of the component \( i \) for the global warming burden, kg CO\(_2\)/kg \( i \)
- \( m_{\text{product}} \): mass flow of product \( i \), kg
Design for Sustainability and GREENSCOPE Evaluation
Maleic Anhydride Production Process: Conventional Approach

- MA is produced at industrial scale for applications in coatings and polymers:
  - Unsaturated polyester resin, production of fumaric and malic acid, lube oils as an additive, and maleic copolymers
- Currently, two main production routes:
  - Benzene oxidation or other aromatic compounds
    - Environmental concerns, increasing price of benzene
  - Gas phase oxidation of n-butane
    - Availability of n-butane as a feedstock
    - Nonrenewable material
Maleic Anhydride Production Process: Conventional Approach

• Major components in the MA process
  – Feedstock supply (benzene or n-butane), catalyst manufacture, air compression, reaction system, MA recovery/refining and off gas incineration

• Catalyst fixed bed reactor
  – Vanadium-phosphorus-oxide (VPO) for n-butane
  – \( V_2O_5\)-MoO\(_3\) for benzene

• Multiple parallel and in-series oxidization reactions not only to MA, but also to CO and CO\(_2\)

• A large amount of water is produced

• Highly exothermic reactions
Maleic Anhydride Production Process: A Bio-based Approach

• Feedstock: Bio-butanol (2G≤) with air
  – Gas phase reaction, no solvent used

• Catalyst fixed bed reactor
  – Catalyst: Vanadyl pyrophosphate
  – Air in excess is compressed, heated and mixed with the feedstock before being fed to the reactor
  – 3 s residence time

• T: 340 °C; P: 1 bar

• Multiple oxidization reactions:
  – MA, CO, CO₂, H₂O, phthalic anhydride, acetic acid, acrylic acid, and other “lights”, such as formaldehyde, butenes, lighter hydrocarbons
Maleic Anhydride from Bio-butanol
CHEMCAD Process Simulation

- Bio-butanol
- 98% butanol conversion
- Products: maleic anhydride, acetic acid, acrylic acid,
- phthalic anhydride, formalin
- Utilities: steam, electricity, cooling water
- Liquid, & air releases
Sustainability Assessment & Design: GREENSCOPE Tool

• Sustainability quantitative assessment
• Individual or multiple process comparisons
• Key factors, areas for improvements, optimal tradeoffs
Efficiency Indicator Results

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Description</th>
<th>Sust. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. AE_i</td>
<td>Atom economy</td>
<td>5.8</td>
</tr>
<tr>
<td>7. MI_v</td>
<td>Value mass intensity</td>
<td>0</td>
</tr>
<tr>
<td>15. MRP</td>
<td>Material recovery parameter</td>
<td>0</td>
</tr>
<tr>
<td>17. pROI_M</td>
<td>Physical return on investment</td>
<td>99.4</td>
</tr>
<tr>
<td>23. V_water, tot.</td>
<td>Total water consumption</td>
<td>100</td>
</tr>
</tbody>
</table>
### Environmental Indicator Results

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Description</th>
<th>Sust. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (N_{\text{haz. mat.}})</td>
<td>Number of hazardous materials input</td>
<td>75</td>
</tr>
<tr>
<td>6. (HH_{\text{irritation}})</td>
<td>Health hazard, irritation factor</td>
<td>68.5</td>
</tr>
<tr>
<td>10. (SH_{\text{react/dec I}})</td>
<td>Safety hazard, reaction / decomposition I</td>
<td>88.3</td>
</tr>
<tr>
<td>22. (EH_{\text{bioacc.}})</td>
<td>Environmental hazard, bioaccumulation (the food chain or in soil)</td>
<td>89.3</td>
</tr>
<tr>
<td>43. EP</td>
<td>Eutrophication potential</td>
<td>100</td>
</tr>
</tbody>
</table>
Energy Indicator Results

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Description</th>
<th>Sust. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. $R_{SEI}$</td>
<td>Specific energy intensity</td>
<td>98.9</td>
</tr>
<tr>
<td>6. $\eta_E$</td>
<td>Resource-energy efficiency</td>
<td>77.0</td>
</tr>
<tr>
<td>8. $BF_E$</td>
<td>Breeding-energy factor</td>
<td>100.0</td>
</tr>
<tr>
<td>10. $Ex_{total}$</td>
<td>Exergy consumption</td>
<td>0.0</td>
</tr>
<tr>
<td>14. $BF_{Ex}$</td>
<td>Breeding-exergy factor</td>
<td>36.1</td>
</tr>
</tbody>
</table>
Economic Indicator Results

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Description</th>
<th>Sust. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NPV</td>
<td>Net present value</td>
<td>45.9</td>
</tr>
<tr>
<td>8. PBP</td>
<td>Payback Period</td>
<td>92.0</td>
</tr>
<tr>
<td>19. COM</td>
<td>Manufacturing cost</td>
<td>68.0</td>
</tr>
<tr>
<td>23. $C_E$</td>
<td>Specific energy costs</td>
<td>63.1</td>
</tr>
<tr>
<td>33. $C_{pur. air fract.}$</td>
<td>Fractional costs of purifying air</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Life Cycle Inventory Results: GREENSCOPE Tool

<table>
<thead>
<tr>
<th>Compound #</th>
<th>Compound Name</th>
<th>CAS Number</th>
<th>Input kg/h</th>
<th>Output kg/h</th>
<th>Net output waste, kg/h</th>
<th>Net product flow, kg/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-Butanol</td>
<td>71-36-3</td>
<td>2</td>
<td>7412.300</td>
<td>7.376</td>
<td>2.838</td>
</tr>
<tr>
<td>2</td>
<td>Maleic Anhydride</td>
<td>108-31-6</td>
<td>1</td>
<td>0</td>
<td>890.546</td>
<td>890.55</td>
</tr>
<tr>
<td>3</td>
<td>Water</td>
<td>7732-18-5</td>
<td>4</td>
<td>250.000</td>
<td>5488.405</td>
<td>1811.729</td>
</tr>
<tr>
<td>4</td>
<td>Carbon Monoxide</td>
<td>630-08-0</td>
<td>0</td>
<td>0</td>
<td>1017.527</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>Carbon Dioxide</td>
<td>124-38-9</td>
<td>0</td>
<td>0</td>
<td>1598.754</td>
<td>1598.754</td>
</tr>
<tr>
<td>6</td>
<td>Phthalic Anhydride</td>
<td>85-44-9</td>
<td>1</td>
<td>0</td>
<td>1345.182</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>Acrylic Acid</td>
<td>79-10-7</td>
<td>1</td>
<td>0</td>
<td>2617.892</td>
<td>2617.89</td>
</tr>
<tr>
<td>8</td>
<td>Acetic Acid</td>
<td>64-19-7</td>
<td>1</td>
<td>0</td>
<td>1088.059</td>
<td>249.033</td>
</tr>
<tr>
<td>9</td>
<td>Nitrogen</td>
<td>7782-44-7</td>
<td>5</td>
<td>50425.200</td>
<td>50425.206</td>
<td>50425.206</td>
</tr>
<tr>
<td>10</td>
<td>Oxygen</td>
<td>7727-37-9</td>
<td>2</td>
<td>14399.551</td>
<td>6407.793</td>
<td>6407.793</td>
</tr>
<tr>
<td>11</td>
<td>(E)-2-Butene</td>
<td>107-01-7</td>
<td>0</td>
<td>0</td>
<td>509.528</td>
<td>508.586</td>
</tr>
<tr>
<td>12</td>
<td>Formaldehyde</td>
<td>50-00-0</td>
<td>1</td>
<td>0</td>
<td>1090.707</td>
<td>146.153</td>
</tr>
</tbody>
</table>

Utility type Utility flow rate needs, kg/h, m³/h, MJ/h, or kWh/h

<table>
<thead>
<tr>
<th>Utility type</th>
<th>Flow rate needs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium pressure steam @10 barg 184°C, 1/kg</td>
<td>9385.6599</td>
</tr>
<tr>
<td>Moderately low T Refrigerated water, T_in = 5 °C T_out = 15°C, 1/kg</td>
<td>2232940.6935</td>
</tr>
<tr>
<td>Electricity (kWh/h)</td>
<td>1980.1353</td>
</tr>
</tbody>
</table>


A Framework for More Sustainable Supply Chains & Life Cycles

Global sustainability assessment

1. **Raw material acquisition**: removal of feedstocks and energy sources from the planet

2. **Manufacturing**: Valuable product production from the feedstocks and its delivery

3. **Use**: actual use, reuse, and maintenance of the product, energy requirements & releases

4. **Recycling & disposal**, energy requirements & releases, material management options
Global Sustainability: Implementing Improvements at Process Level

- Elimination of waste treatment units, decreasing capital and manufacturing costs
- No energy load for waste treatment units
- Reduce recycling
- Simplify separation / purification systems
Global Sustainability: Implementing Improvements at Process Level

- Reduce resource depletion, feedstock processing and the need for extra raw materials used for intermediate steps
- Reduce # of feed components & increased capital utilization
- Decrease need for separation agents
- Decrease need for upstream energy-related inputs (processes)
Global Sustainability: Implementing Improvements at Process Level

- Less hazardous chemical syntheses: reduction of hazard risks
- Design for energy efficiency: minimize high temperature releases, reduce GHG emissions
Multi-Stakeholder Decision-Making and Conflict Resolution

• A decision-making framework to compute solutions by balancing
  – Conflicting priorities
  – Multiple stakeholders
  – Multiple objectives
• To minimize stakeholder dissatisfactions
• Effective for complex decision-making processes
Case Study: Sustainable Facility Location Selection

• To locate biowaste processing facilities in a geographical region in order to:
  – Minimize transportation
  – Maximize the distance between facilities and urban areas to avoid safety and health concerns
  – Maximize the distance between facilities and watersheds to avoid contamination
  – Minimize capital costs

• Other applications: wind farms, wastewater treatment facilities, landfills, etc.

• Multiple conflicting objectives and stakeholders

• Location of facilities considering priorities of communities, farmers, local/federal agencies, investors, etc.
Case Study: Sustainable Facility Location Selection

- Compromise solutions in terms of stakeholder dissatisfactions
- To provide a mechanism to explore and quantify the effect of opinions on final decisions
- Computing an entire Pareto set is not practical for problems with many competing objectives and stakeholder preferences

- Minimize average dissatisfaction
- A balance between the mean and the worst-case solutions
- Minimize worst dissatisfaction
Integrated U.S. Biorefineries: The Needs For Local or Regional Values

- Energy crops: e.g., switchgrass, miscanthus, etc.
- Agricultural waste (cane bagasse), stover, waste bins, etc.
- Various combinations of raw material and conversion technologies
Remaining Challenges to Advance Sustainability

- Data availability for the calculation or prediction of sustainability using indicators
  - Chemical process heterogeneity
  - New chemical compounds
    - Physicochemical properties
    - Toxicity properties and classification lists
  - Cost
    - Technoeconomic assessment of unconventional equipment
    - Time value variations
- Quantitative social indicators
- Multiproduct allocation for processes and facilities
  - Mass, energy, value
- Legal foundations and the establishment of official methodologies and standards for the assessment of sustainability
Conclusions

- Sustainable development applied to chemical process engineering
- Performance indicators for designing sustainable processes at any scale or design phase
- GREENSCOPE quantifies results of sustainable practices
  - Modifications in the type and magnitude of goods and services
  - Preventing and minimizing all types of releases
  - Manufacturing the desired product & maximizing its economic benefits
- More Sustainable Supply Chains
  - Global sustainable processes and products (no burden shift)
  - Connect the LCI with the decision-makers
Acknowledgments

✓ Drs. Michael A. Gonzalez & Raymond L. Smith, GREENSCOPE Co-developers
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✓ Drs. José M. Ponce & Agustín J. Castro, Universidad Michoacana de San Nicolás de Hidalgo
✓ Comité Organizador del III RTB y XII REMBIO
Student Opportunities at the EPA

Fellowships and post-doctoral opportunities:

• American Association for the Advancement of Science (AAAS) Science and Technology Policy Fellowships

• Association of Schools and Programs of Public Health (ASPPH)/EPA Environmental Health Fellowship Program

• EPA Office of Research and Development Post-Doctoral Research Program

• Greater Research Opportunities (GRO) Undergraduate Fellowships

• National Academy of Sciences/National Research Council Resident Research Associateship Program

• Oak Ridge Institute for Science and Education (ORISE) Fellowships

• Presidential Management Fellows (PMF) Program

• Science to Achieve Results (STAR) Fellowships for Graduate Environmental Study
National Academy of Sciences/National Research Council Resident Research Associateship Program

• Post-doctoral, mid-career technical professionals, and Faculty at the assistant Professor level
• To work as visiting scientists at federal laboratories, including EPA, for periods of up to three years
• Opportunities for engineers, ecologists, mathematicians, statisticians, as well as other scientific backgrounds, for the future.
• The Program offers an attractive stipend, health insurance, and travel allowance
• Open to U.S. citizens, permanent residents and non-U.S. citizens
• [https://www.epa.gov/careers/fellowships-scholarships-and-post-doctoral-opportunities#nas](https://www.epa.gov/careers/fellowships-scholarships-and-post-doctoral-opportunities#nas)
Oak Ridge Institute for Science and Education (ORISE) Internships, Scholarships and Fellowships

- Internships and research project training opportunities funded by EPA and by other government and private sector organizations
- Opportunities are available year-round to science and engineering undergrads, grad students, recent grads, post-docs, faculty
- Open to U.S. citizens, permanent residents and non-U.S. citizens
Thanks!

Questions?

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Current Job Openings, Internships, Fellowships, Scholarships and Other Student Opportunities:

https://www.epa.gov/careers

• For Undergraduate, Post-BS/MSc/PhD Fellows