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SCIENCE AND TECHNOLOGY FOR SUSTAINABILITY PROGRAM
Policy and Global Affairs

Chemical Process Indicators for Sustainability Assessment and Design

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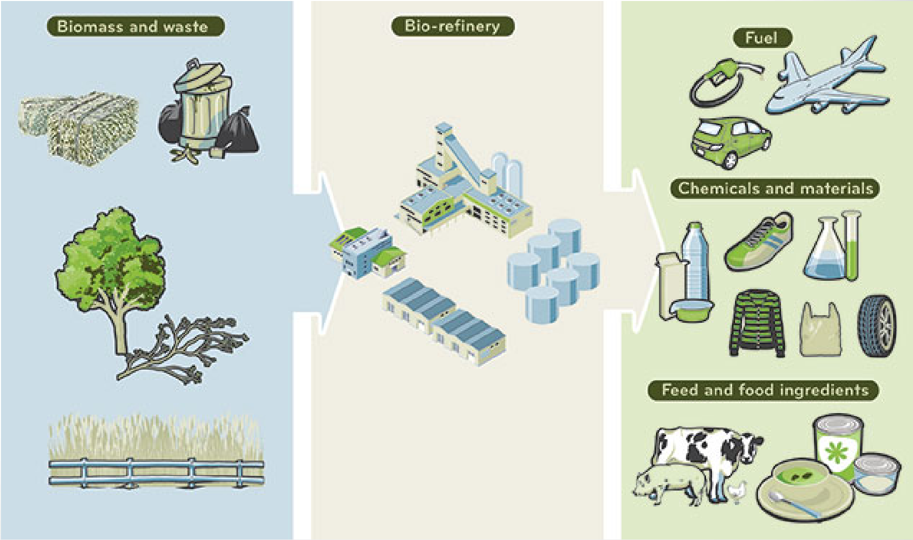
Agenda

- Sustainability and Chemical Processes
- Sustainability Indicators
- GREENSCOPE Sustainability Evaluation Tool
- GREENSCOPE Evaluation and Case Study
- Challenges, Needs, and Opportunities to Advance Sustainability at Process Level

Sustainability and Chemical Processes



http://biconsortium.eu/sites/biconsortium.eu/files/pictures/Bio_Based_Basic_model.jpg

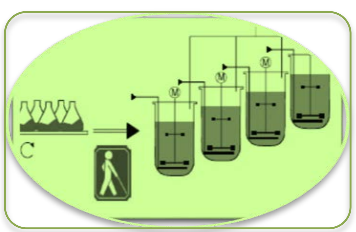
Sustainability for Chemical Processes

Current environmental and social aspects that may be affected by industry

- Renewable &/or bio-based products & feedstocks: meet economic, social, and environmental benefits

Join efforts to incorporate sustainability principles

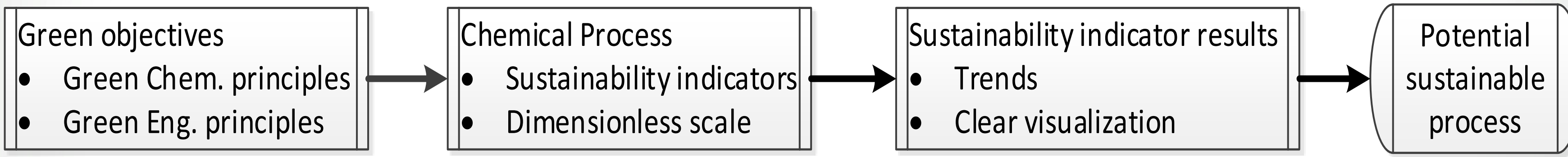
- Efficient renewable material transformation
- Less energy consumption and waste (nonhazardous) generation
- Clean processes, optimum social and economic benefits
- Life cycle assessment considerations



Sustainability from the lab to the manufacturing plant

- Inexpensive starting materials
- High-yield and easy isolation of pure products

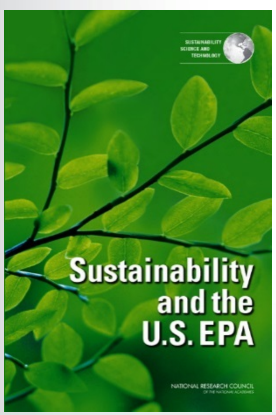
Quantitative Sustainability Assessment



Qualitative Approaches
Apply all of them?
Levels of implementation?
A "win-win" situation?
Multiobjective function

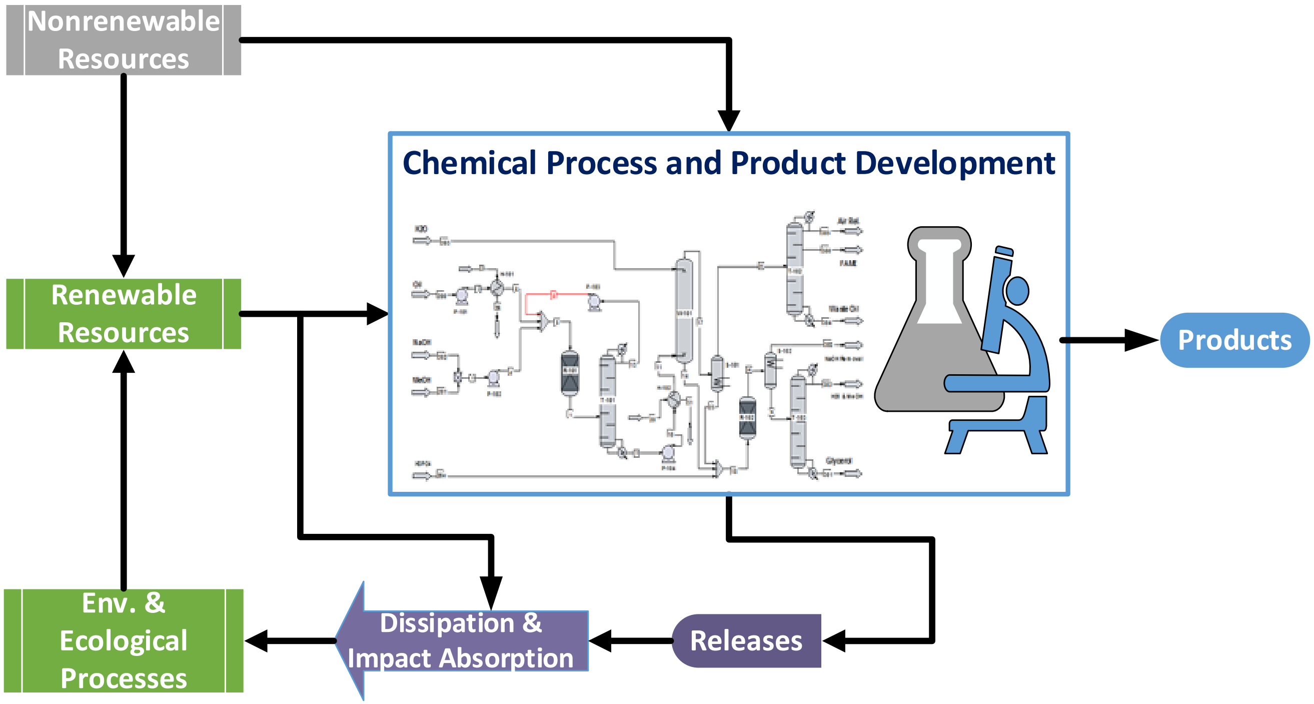
Quantitative Approaches
Is this a sustainable process?
How sustainable is it?
Realistic limitations
Scale for measuring sustainability

Sustainability Criteria
Process areas for improvements
Identification of key factors (SA)
Multi-criteria decision making
Optimal tradeoff



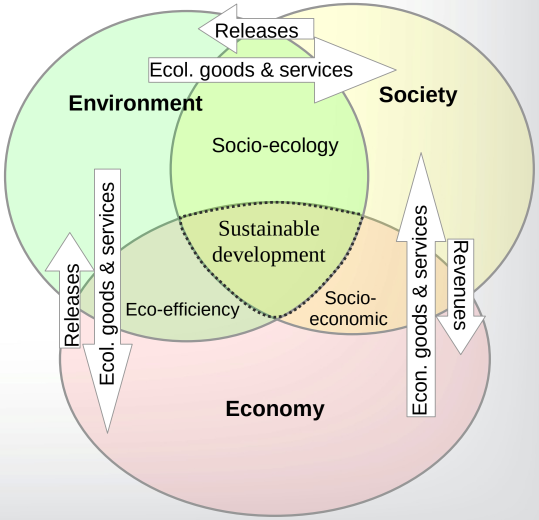
- NAS committee on incorporating sustainability in the U.S. EPA
  - Integrate sustainability assessment and management into management and policy decisions
  - Assessments in terms of a trade-off and synergy analysis
- From qualitative to quantitative definitions
- To evaluate & improve sustainability at early process design stages

Sustainable Process Design Procedure



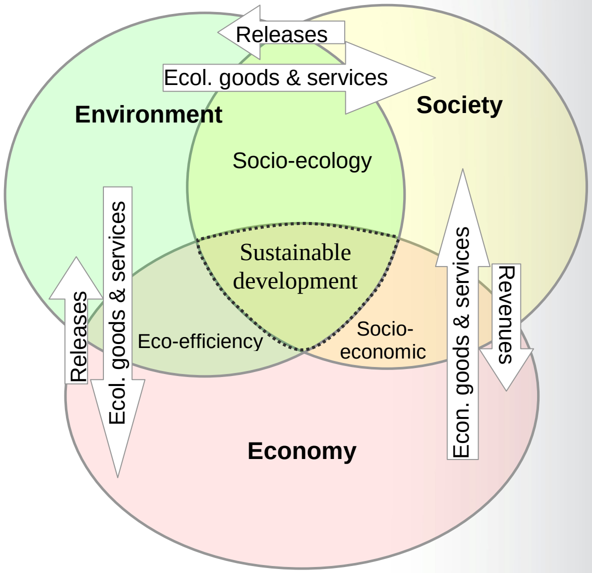
- Support decision-makers to determine whether a process is becoming more or less sustainable
  - Are we doing relatively good / bad?
- What benchmarks to use?
- How close are we to achieving absolute targets?

Sustainability Indicators



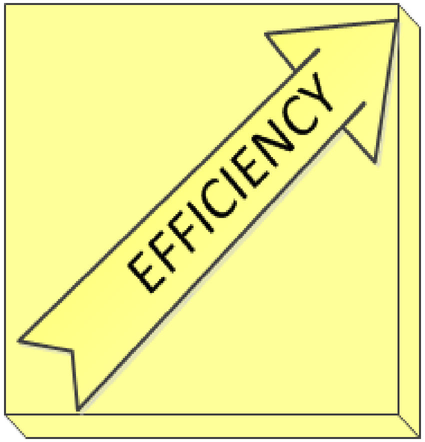
Chemical Process Indicators

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



- Four areas for promoting & informing sustainability
  - Integrated evaluation & decision-making @ design level
    - Environmental, Efficiency, Economics, Energy (4E's)
  - Comprehensive and systems-based indicators for use in process design

The GREENSCOPE Tool



- Clear, practical, and user-friendly approach
- Monitor and predict sustainability at any stage of process design
- Currently developed into a spreadsheet tool, capable of calculating 139+ different indicators
- Stakeholders can choose which indicators to calculate
- Decision-makers can redefine absolute limits to fit circumstances

GREENSCOPE Sustainability Framework

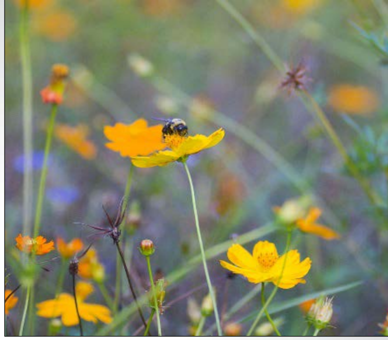
- Identification and selection of two reference states for each sustainability indicator:
  - Best target: 100% of sustainability
  - Worst-case: 0% of sustainability

- 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

$$\%\ \text{Sustainabilty Score} = \frac{(\text{Actual-Worst})}{(\text{Best-Worst})} \times 100\%$$

Environmental Indicators



- 66 indicators
- Health & safety hazards: operating conditions and operation failures
- Impact of components utilized in the system and releases
- Risk assessment & ecosystem services evaluation
- Integrated to life cycle assessment
- 100% sustainability, best target, is no releases of pollutants and no hazardous material use or generation
- 0% sustainability, worst cases, all inputs are classified as hazardous, and/or all generated waste for each potential *EHS* hazard is released out of the process

Environmental Indicators: Example

Safety hazard, fire explosion

$$SH_{\text{fire/explosion}} = \frac{\text{Probable energy potential for reaction with } O_2}{\text{Mass of product}}$$

$$SH_{\text{fire/explosion}} = \frac{\left(-\Delta H_{c,i} \times 10^{4\times IndVal_i - 4}\right) \dot{m}_i}{\dot{m}_{\text{product}}}$$

If ΔT_{flash} is known

$$IndVal_i = \begin{cases} -0.005\Delta T_{\text{flash},i} + 1.0 & \text{if } 0 < \Delta T_{\text{flash}} < 200 \\ 1 & \text{if } \Delta T_{\text{flash}} \le 0 \\ 0 & \text{if } \Delta T_{\text{flash}} \ge 200 \end{cases}$$

Elseif R_{code} is known

$$IndVal_i = \begin{cases} 1 & \text{if } R_{\text{code}} = 12,15,17,18 \\ 0.875 & \text{if } R_{\text{code}} = 11,30 \\ 0.75 & \text{if } R_{\text{code}} = 10 \\ 0 & \text{if } R_{\text{code}} = \text{other} \end{cases}$$

Elseif NFPA – f is known

$$IndVal_i = \begin{cases} 1 & \text{if NFPA-flamm=4} \\ 0.833 & \text{if NFPA-flamm=3} \\ 0.667 & \text{if NFPA-flamm=2} \\ 0.5 & \text{if NFPA-flamm=1} \\ 0 & \text{if NFPA-flamm=0} \end{cases}$$

end

Sustainability value	
Best, 100%	Worst, 0%
0 kJ/kg	All combustion enthalpy of each process substance is released

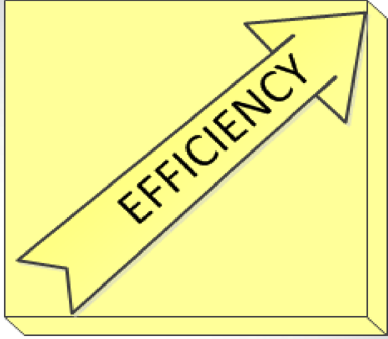
ΔH_c: combustion enthalpy, kJ/kg

ΔT_{flash}: temperature difference between the standard flash point and process temperature, °C

R_{code}: Risk phrases of European community

NFPA-f: flammability hazard class according to the U.S. National Fire Protection Agency (NFPA)

Efficiency Indicators



- 26 indicators
- Amount of materials and inputs required to generate the desired product (reaction) or complete a specific process task (e.g., separation)
- Mass transfer operations have implicit influence in the amount of energy demand, equipment size, costs, raw materials, releases, etc.
- Efficiency indicators connect material input/output with the product or intermediate generated in the process or operating unit

Efficiency Indicators: Example

Actual atom economy

$$AAE = AE \times \varepsilon$$

$$AE_i = \frac{\left[(\text{Molecular weight}) \times (\text{stoichiometric coefficient})\right]_i}{\sum_{\text{reagents}} \left[(\text{Molecular weight}) \times (\text{stoichiometric coefficient})\right]_{\text{reagent}}}$$

$$\varepsilon = \frac{\text{Mass of product}}{\text{Theoretical mass of product}}$$

$$AAE = \frac{(\beta \times \text{MW})_{\text{product}} \times m^{\bullet}_{\text{product}}}{\sum_{i=1}^{I} (\alpha \times \text{MW})_{\text{reagent, } i} \times \frac{m^{\bullet \text{in}}_{\text{limit. reagent}}}{\text{MW}_{\text{limit. reagent}}} \times \frac{\beta_{\text{product}}}{\alpha_{\text{limit. reagent}}} \times \text{MW}_{\text{product}}}$$

Sustainability value	
Best, 100%	Worst, 0%
1	0

$m^{\bullet}_{\text{product}}$: mass flow of product *I* , kg/h
$m^{\bullet \text{in}}_{\text{limit. reagent}}$: input mass flow rate of the limiting reagent, kg/h
MW_i: molecular weight of the component *i*, kg/kmol
α_i: stoichiometric coefficient of the reagent *i*
β_{product}: stoichiometric coefficient of the desired product

Value mass intensity

$$MI_{\text{V}} = \frac{\text{Total mass input}}{\text{Sales revenue or value added}}$$

$$MI_{\text{V}} = \frac{\sum_{i=1}^{I} m^{\bullet \text{in}}_{m,i}}{S_m}$$

$$S_m = \sum_{i=1}^{I} m^{\bullet}_{m,\text{ product } i} \times C_{m,\text{product } i}$$

Sustainability value	
Best, 100%	Worst, 0%
1	40

$m^{\bullet \text{in}}_{m,i}$: input mass flow rate of the limiting reagent, kg/h
annual mass flow of substance *i* in year *m*, kg/yr
S_m: total income from all sales in year *m*, \$
$C_{m,i}$: cost of material *i* in year *m*, \$/kg
$m^{\bullet}_{\text{m, product, } i}$: : annual mass flow of product *i* in year *m*, kg/yr

Economic Indicators

- 33 indicators
- A sustainable economic outcome must be achieved for any new process technology or modifications
- Based in profitability criteria for projects (process, operating unit),
  - May or may not account for the time value of money
  - Benefit-cost analysis
- Indicators supported in cost criteria:
  - Processing costs: capital cost, manufacturing cost
  - Process input costs: raw material cost, utility costs
  - Process output costs: waste treatment costs

Economic Indicators: Example

Net present value

$NPV =$ The total of the present value of all cash flows minus the present value of all capital investments

$$NPV = \sum_{m=1}^{n} \text{PWF}_{cf,m}\left[\left(S_m - COM_m - d_m\right)\left(1-\Phi\right) + \text{rec}_m + d_m\right] - \sum_{m=-b}^{n} \text{PWF}_{v,m} TCI_m$$

$$S_m = \sum_{i=1}^{I} \dot{m}_{m,\text{ product } i} \times C_{m,\text{product } i}$$

$$COM_m = 0.280 FCI_{L,m} + 2.73 C_{OL,m} + 1.23\left(C_{UT,m} + C_{WT,m} + C_{RM,m}\right)$$

$$d_m = 0.1 FCI_L$$

$$\text{rec}_m = \begin{cases} C_{\text{Land}} + WC + FCI_L - \sum_{m=1}^{n} d_m & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}$$

$$TCI_m = \text{C}_{\text{Land},m} + FCI_{L,m} + WC_m$$

$$FCI_L = C_{TM} = 1.18 \sum_{i=1}^{u} C_{BM,i}$$

$$C_{BM,i} = C^o_{p,i} F_{BM,i}$$

$$C_{OL} = 4.5 N_{OL} \times \left(\text{annual salary}\right)$$

$$N_{OL} = \left(6.29 + 31.7P^2 + 0.23 N_{np}\right)^{0.5}$$

$$N_{np} = \sum \text{Equipment}$$

Sustainability value	
Best, 100%	Worst, 0%
NPV @ discount rate (r_d)= 0%	*NPV* @ r_d= minimum acceptable rate of return (*MARR*)=40% for very high risk projects

n: life of the plant or equipment, yr
$\text{PWF}_{cf,m}$: the selected present worth factor
S_m: total income from all sales in year *m*, \$
COM_m: cost of manufacture without depreciation, \$
FCI_L : Fixed capital investment without including the land value
d_m: depreciation charge. Here, it is assumed as 10% of the FCI_L evaluated in year *m*, however it can be estimated by different methods
Φ: fixed income tax rate given by the IRS
rec_m: salvage-value recovered from the working capital, land value, and the sale of physical assets evaluated at the end of the plant life. Often this salvage value is neglected, \$

Energy Indicators

- 14 indicators
- Different thermodynamic assessments for obtaining an energetic sustainability score
  - Energy (caloric); exergy (available); emergy (ecosystem services)
- Zero energy consumption per unit of product is the best target (more products per unit of consumed energy)
- Most of the worst cases do not have a predefined value
  - They depend on the particular process or process equipment
  - The designer has to choose which value is unacceptable
  - Some worst cases can be assigned by taking the lowest scores found through comparing several sustainability corporate reports

Energy Indicators: Example

Exergy intensity

$$R_{Ex} = \frac{\text{Net exergy used}}{\text{Mass of product}}$$

$$R_{Ex} = \frac{\dot{Ex}^{in} - \dot{Ex}_{lost}}{\dot{m}_{product}}$$

$$\dot{Ex}^{in} = \left[\dot{Ex}(\text{physical}) + \dot{Ex}(\text{chemical})\right]_{\text{input flows}} + \dot{Ex}(\text{work}) + \dot{Ex}(\text{heat})$$

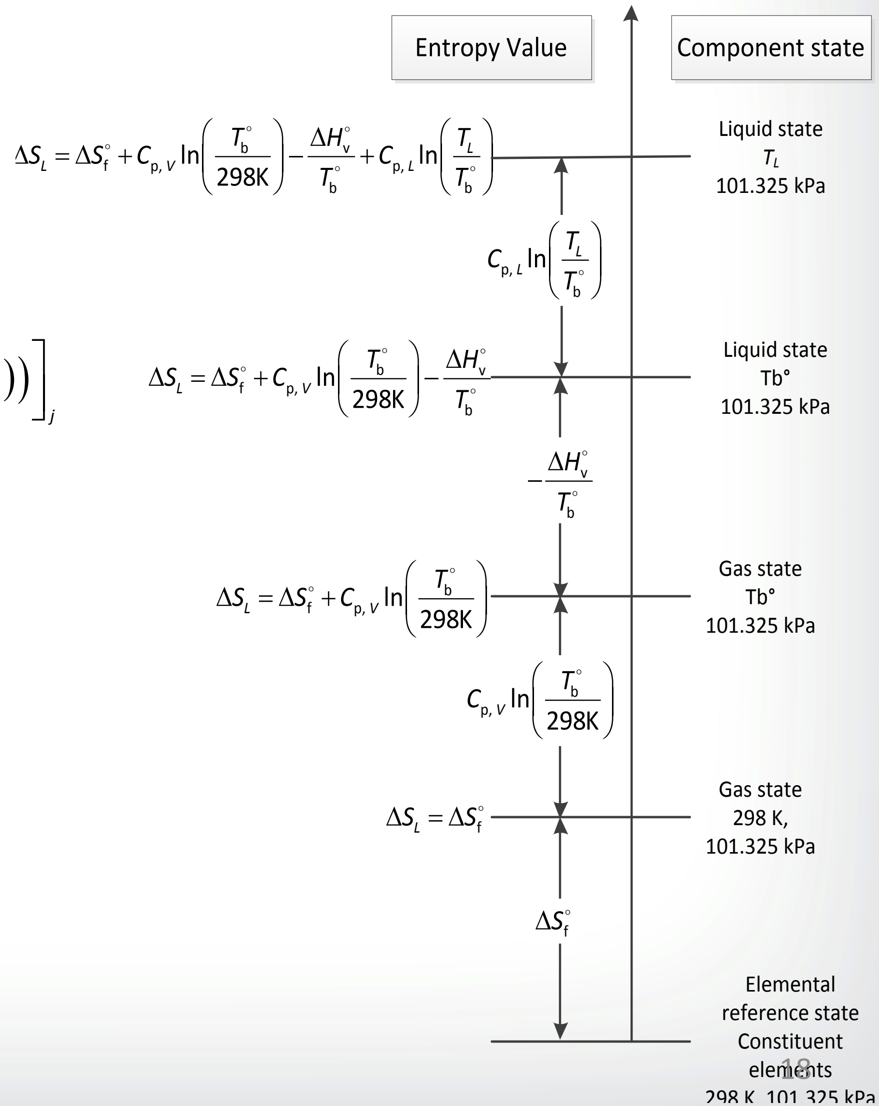
$$\dot{Ex}^{in} = \sum_{j=1}^{J} \dot{m}_j^{in}\left(\Delta H - T_0 \Delta S\right)_j + \sum_{j=1}^{J}\left[\sum_{i=1}^{c} \dot{n}_i \sum_{i=1}^{c}\left(x_i Ex_i^{\circ ch} + RT_0 x_i \ln(x_i)\right)\right]_j + \sum_{k=1}^{K'} \dot{W}_k + \sum_{k=1}^{K} \dot{Q}_k \left(1 - T_0 / T_{*,k}\right)$$

$$\dot{Ex}_{lost} = T_0 \dot{S}_{generated}$$

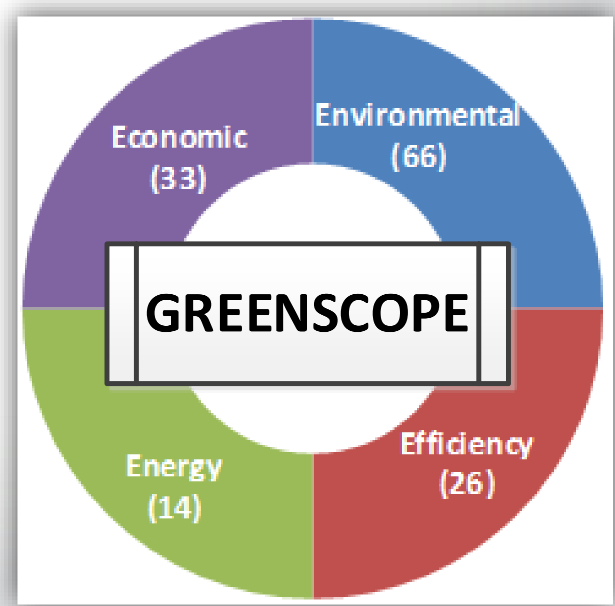
$$\dot{S}_{generated} = \sum_{j=1}^{J} \dot{m}_j^{in} \times \Delta S_j - \sum_{j=1}^{J'} \dot{m}_j^{out} \times \Delta S_j - \sum_{k=1}^{K} \frac{\dot{Q}_k}{T_0}$$

$$\Delta S_{L,j} = \sum_{i=1}^{c} x_{i,j} \Delta S_{L,ij} + \Delta S_{L,j\ \text{mix}} \qquad \Delta S_{V,j} = \sum_{i=1}^{c} y_{i,j} \Delta S_{V,ij} + \Delta S_{V,j\ \text{mix}}$$

Sustainability value	
Best, 100%	Worst, 0%
0	Max Ex_{total}/kg product

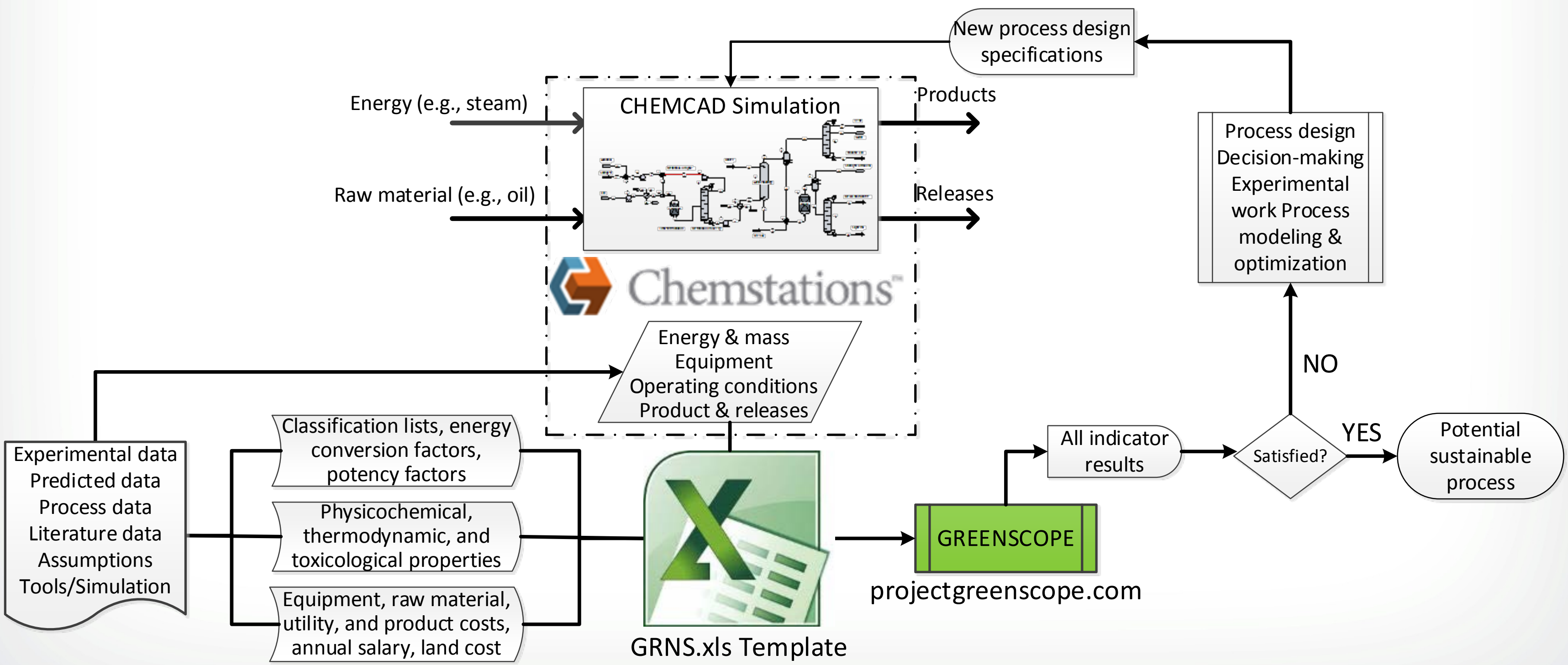


GREENSCOPE Evaluation and Case Study



GREENSCOPE Tool: A Demonstration Case Study

- Sustainability quantitative assessment
- Individual or multiple process comparisons: Waste cooking oil, USDA model, Recycling unconverted oil, Hexane extraction
- Key factors, areas for improvements, optimal tradeoffs

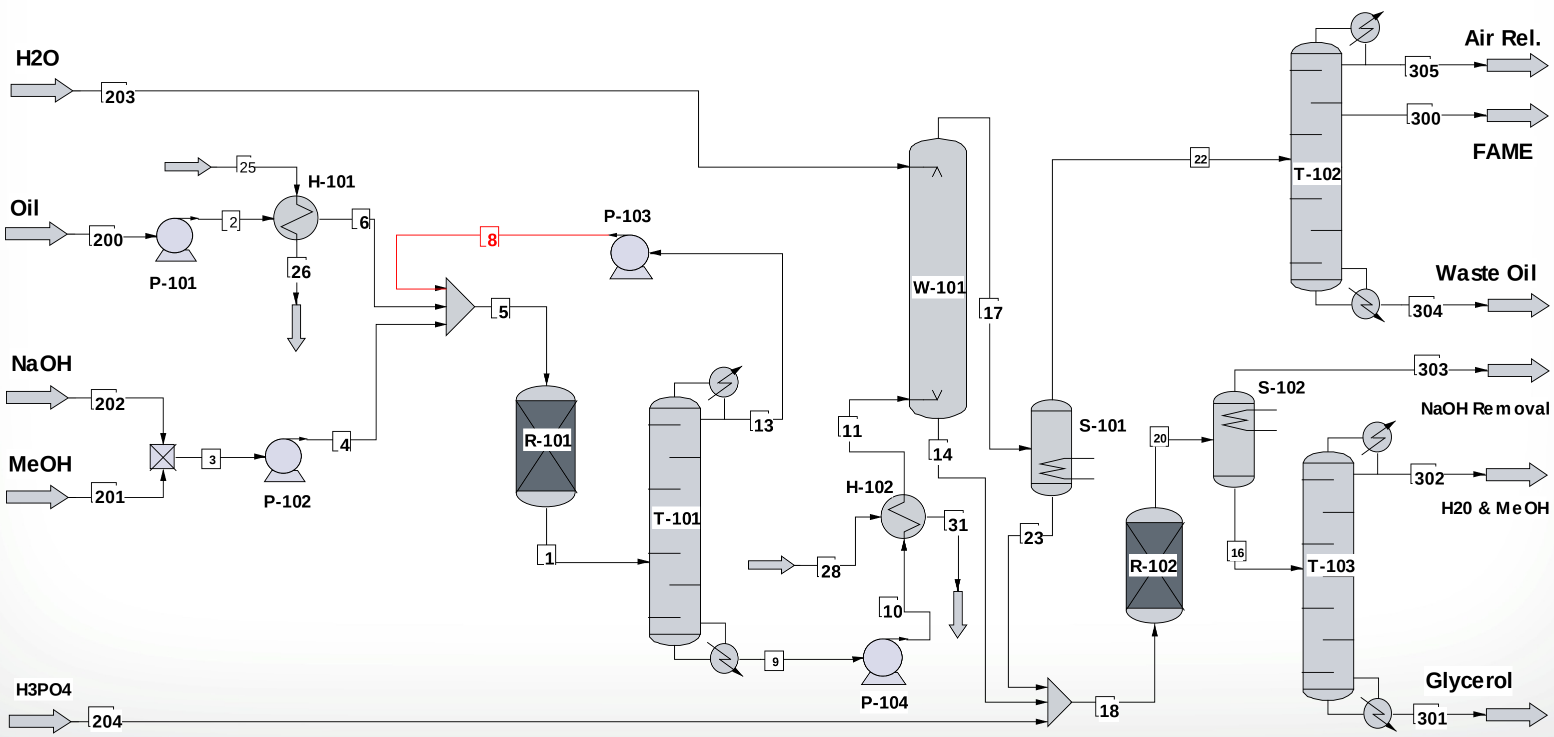


CHEMCAD Simulated Chemical Process File

- Pure soybean oil
- 95% Oil conversion
- 1 Ton FAME/h
- 99.60% Purity

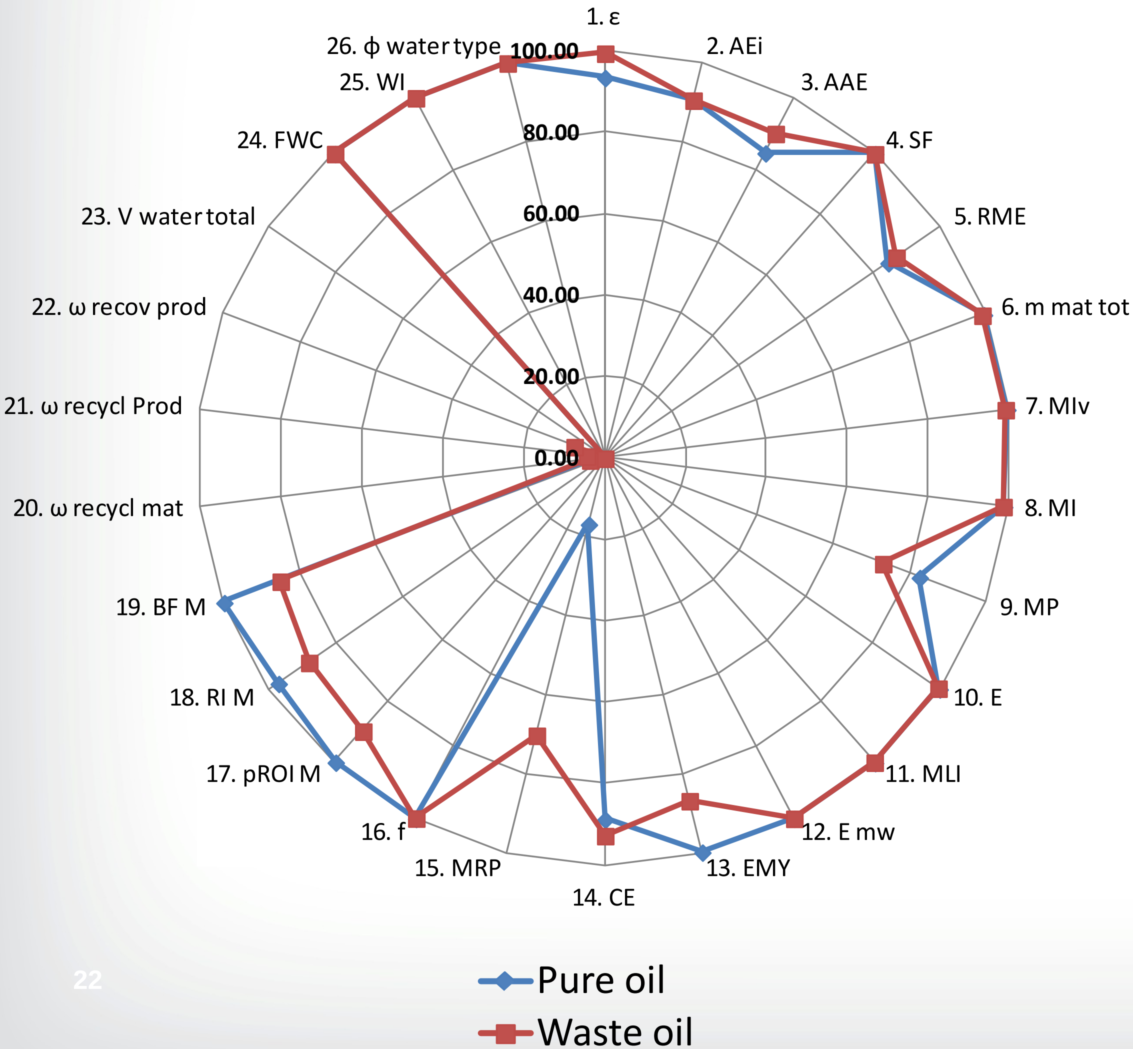
- 0.1 Ton Glycerol/h
- Utilities: steam, electricity, cooling water
- Solid, liquid, & air releases

I N P U T S



O U T P U T S

Efficiency Indicator Results



Indicator	Description	Sust. (%) Pure Oil	Sust. (%) Waste Oil
2. AE_i	Atom economy	90.6	90.6
7. MI_v	Value mass intensity	99.5	99.1
15. MRP	Material recovery parameter	16.7	70.0
17. $pROI_M$	Physical return on investment	99.8	89.6
25. WI	Water intensity	100	100

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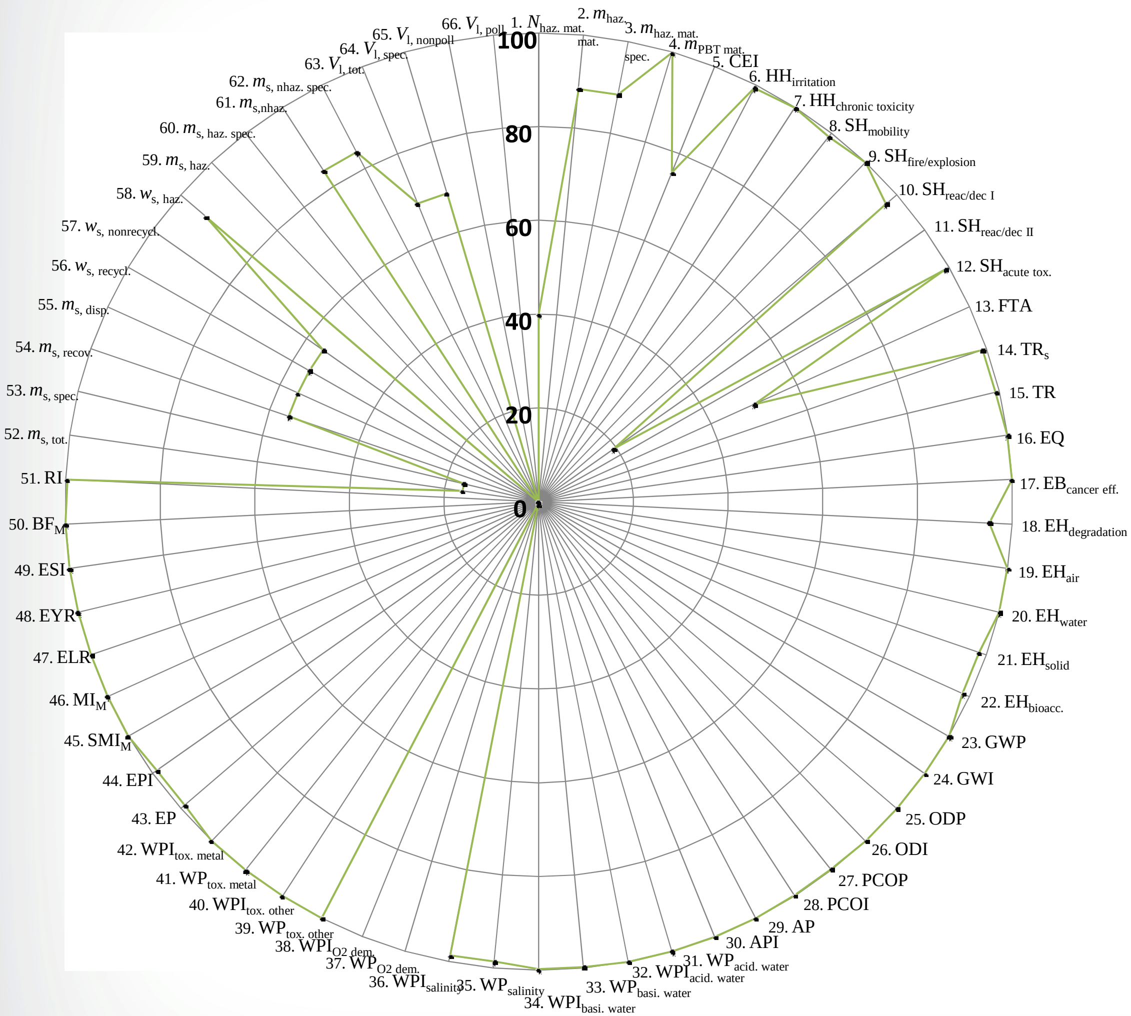
Environmental Indicator Results



Indicator	Description	Sust. (%)
1. $N_{haz. mat.}$	Number of hazardous materials input	40.00
6. $HH_{irritation}$	Health hazard, irritation factor	99.31
10. $SH_{reac/dec I}$	Safety hazard, reaction / decomposition I	97.00
22. $EH_{bioacc.}$	Environmental hazard, bioaccumulation (the food chain or in soil)	98.34
27. PCOP	Photochemical oxidation (smog) potential	99.83
32. $WPI_{acid. water}$	Aquatic acidification intensity	99.88
38. $WPI_{O2 dem.}$	Aquatic oxygen demand intensity	0.60
43. EP	Eutrophication potential	98.89

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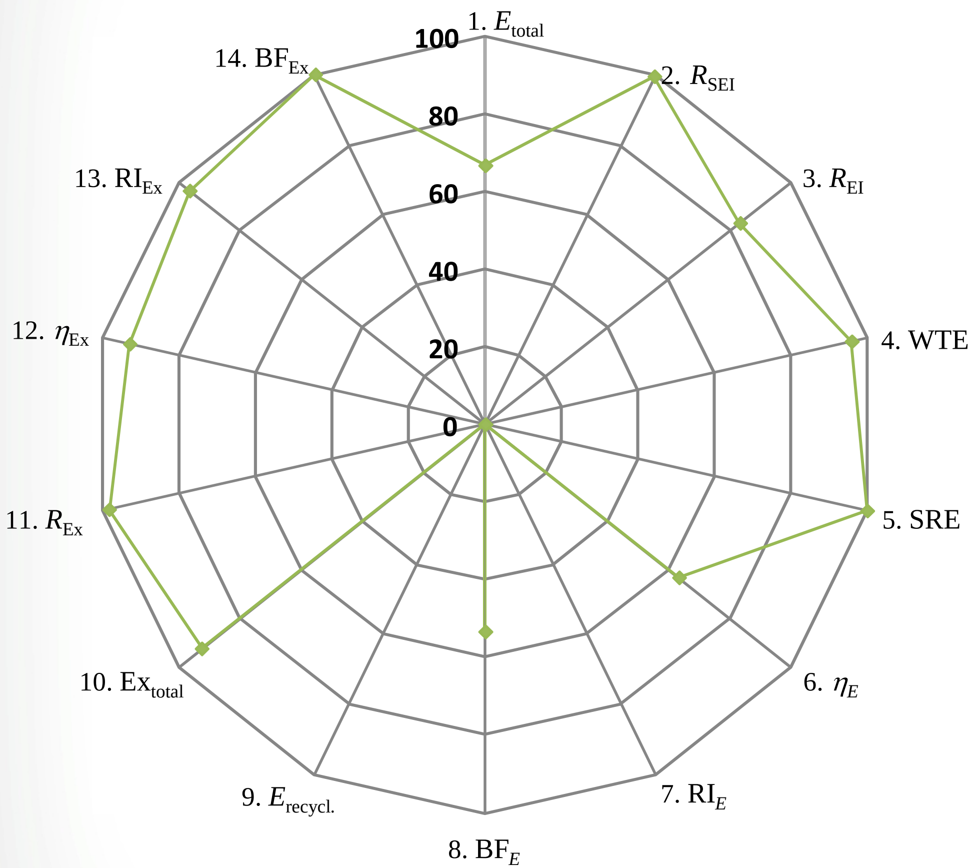
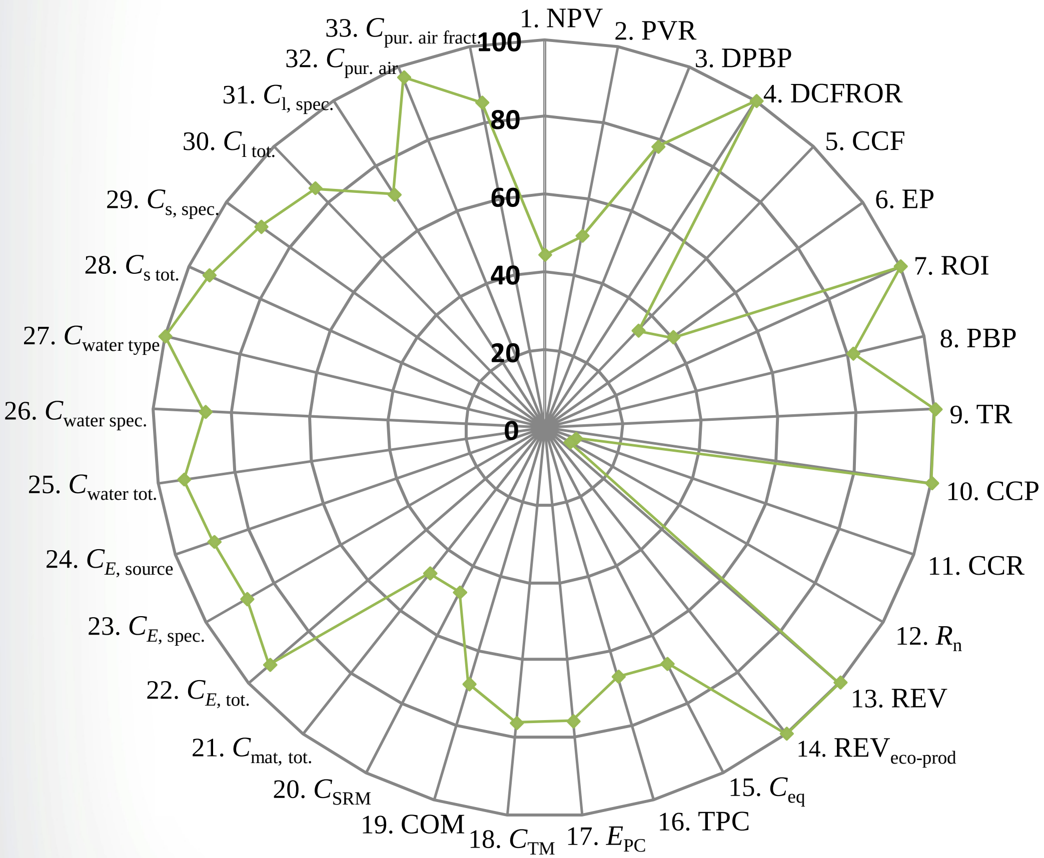
Energy Indicator Results



Indicator	Description	Sust. (%)
2. R_{SEI}	Specific energy intensity	99.49
6. η_E	Resource-energy efficiency	63.26
8. BF_E	Breeding-energy factor	53.38
10. Ex_{total}	Exergy consumption	92.59
14. BF_{Ex}	Breeding-exergy factor	100.00

Economic Indicator Results



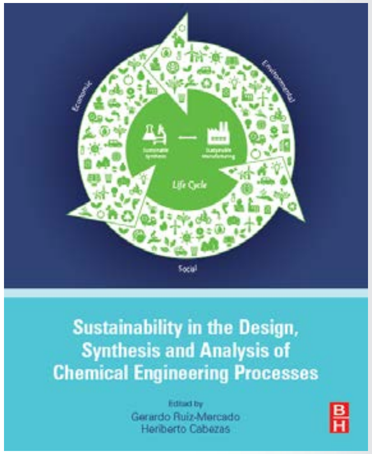
Indicator	Description	Sust. (%)
1. NPV	Net present value	44.52
8. PBP	Payback Period	81.10
19. COM	Manufacturing cost	68.70
23. $C_{E,\ spec.}$	Specific energy costs	88.07
33. $C_{pur.\ air\ fract.}$	Fractional costs of purifying air	85.26

Remaining Challenges to Advance Sustainability at Process Level

- 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
    - Capital costs 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

Needs and opportunities related to sustainability

- To incorporate sustainability at the early stages of a project life and at the early educational levels (New book Ruiz-Mercado and Cabezas (eds.), Elsevier)



  – Sustainable chemical and products by design
  – Dynamic systems
  – Process control and optimization (Dr. F. Lima, WVU)
    - process control with sustainability assessment tools for the simultaneous evaluation and optimization of process operations
  – Multi-stakeholder decision-making (Dr. V. Zavala, U Wisconsin-Madison)
    - Design and analysis of sustainable supply chains
- To integrate life cycle considerations (assessment, inventory) at process development level
- Sustainability regulations at state, country, and international levels
  – Not just greenhouse gases

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References

- Ruiz-Mercado, G. J.; Gonzalez, M. A.; Smith, R. L., Expanding GREENSCOPE beyond the Gate: A Green Chemistry and Life-Cycle Perspective. *Clean Tech. & Env. Policy* 2014, 16, (4), 703–713.
- Ruiz-Mercado, G. J.; Gonzalez, M. A.; Smith, R. L., Sustainability Indicators for Chemical Processes: III. Biodiesel Case Study. *Ind. & Eng. Chem. Res.* 2013, 52, (20), 6747–6760.
- Ruiz-Mercado, G. J.; Smith, R. L.; Gonzalez, M. A., Sustainability Indicators for Chemical Processes: II. Data Needs. *Ind. & Eng. Chem. Res.* 2012, 51, (5), 2329-2353.
- Ruiz-Mercado, G. J.; Smith, R. L.; Gonzalez, M. A., Sustainability Indicators for Chemical Processes: I. Taxonomy. *Ind. & Eng. Chem. Res. 2012*, 51, (5), 2309-2328.

Thanks!

Questions?

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