Research Group ENVOC

Clean Technology:
Sustainability Analysis through
Exergetic Life Cycle Assessment

Prof. Dr. Ir. J. Dewulf
Clean Technology vs. Environmental Technology:

- **Environmental technology** = end-of-pipe technology = clean up technology
  
e.g. wastewater treatment plant

- **Clean technology** = preventive approach through better design of the production process itself
  
→ need for thorough process analysis

→ thermodynamic analysis of process
Sustainable Development:

“Development which meets the needs of the present without compromising the ability of future generations to meet their own needs.”

Brundtland definition

Practical Approach:

Quantitative sustainability assessment of production processes based on second law thermodynamics (generation of entropy and loss of exergy)
Exergy-Based Efficiency and Renewability Assessment of Biofuel Production

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Key for cleaner processes: better resource use

Resources = the motor for (clean) technology
No resources, no economy ...

Sustainable resource management is necessary:
- Limited availability
- Growing population
- Growing demand per capita
- Economic importance
- Geopolitical importance

Need for a sustainable resource management tools
Critical issues in resource management
Guideline 1 in resource management:

*Look at the whole supply chain*
Setting system boundaries ...  

Hydrogen: clean fuel ???
Guideline 2 in resource management:

*Make a fair allocation of all resources to the different products*
Guideline 3 in resource management:

*No resource management without a proper quantification method*
COWI Report for European Commission - DG Environment (March 2002):

Concepts for Resource Management for a Sustainable Use of Resources

**Concepts**
- Carrying capacity
- Physical measures
- Thermodynamics
- Economics-based

**Indicators**
- Environmental Space
- Total Material Requirement
- Exergy
- Green GNP
What basis to be chosen for integrated resource mgt?


*Sustainable technology development:*
*If emissions are a bit under control:*
- *Economically sound*
- *Thermodynamically sound*

**Idea:** take thermodynamics as a base for resource management that enables:
- Overall resource input assessment
- Overall resource efficiency assessment
First law and Second law ...
What if our world were an infinite hazy desert? The sand and air are warm, an ocean of energy – energy everywhere. But if you try to use it, it doesn’t work. A landscape of uniformity, nothing concentrated, nothing unique.
Fortunately, the world we live in is rich and varied, with energy existing in a panorama of forms in an array of concentrated pockets and flows.
Energy can be used and work performed when a substance that is different from its surroundings is allowed to equilibrate.

**Resources**

are energy and matter that exist out of equilibrium with the environment.
Exergy is a measure of work potential or disequilibrium from the environment. While exergy can be destroyed, energy cannot. Exergy is the useful portion of energy. Exergy is what most mean when they say energy.
How are these forms of exergy found on our planet, and how much is there?
Primary exergy resources

- Galactic Radiation (2.7 K)
- Lunar gravitation
- Solar radiation
- Solar gravitation

Biosphere

Wind and waves
- One third of wind exergy is within the surface boundary layer.
- Global average wind speed at 50m is 6.6 m/s, providing 330 W/m².
- 60 TW ocean waves dissipate to 3 TW shore waves.
- Open coast wave energy varies from 10-100

Geothermal heat
- Nuclear decay and spontaneous fission generate 30 TW thermal energy but energy conduction and convection is about 45 TW, cooling the core.
- With Q = ∼0.7 at 40 km deep, exergy flow is 32 TW.

Photosynthesis
- 65 TW land (below) and 25 TW ocean productivity.
- Land residence time is 10 years, ocean is 1 month.
- Solar to plant matter efficiency is about 0.5-1%.
- Plant specific chemical exergy is 12-20 MJ/kg.

Ocean tides
- Lunar tides represent 70% of dissipation.
- 2.5 TW dissipate on shallows and shelves, 1.0 TW dissipate in deep ocean.
- 10 kJ for each m² of ocean surface and m of tidal range.

Precipitation
- Average precipitation is 18 Tg/s.
- Total flux is 25 TW gravitational and 19 TW chemical.
- Global average specific gravitational exergy is 6.6 kJ/kg and specific chemical exergy is 4.9 kJ/kg.
But also stored resources:

**Energy:**
- fossil fuels (gas, oil, coal)
- nuclear ores

**Materials:**
- Minerals
- Metal ores
Exergy destruction for energy services

- 18 TW global exergy use.
- Fossil fuels comprise 65% of exergy use.
2nd law of thermodynamics:
‘all real processes generate entropy’
‘all real processes generate loss of work potential’
<table>
<thead>
<tr>
<th>Resource</th>
<th>Exergy value or calculation method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta$ in kJ$<em>{exergy}$/kJ$</em>{energy}$</td>
</tr>
<tr>
<td>Potential energy</td>
<td>$\beta = 1$</td>
</tr>
<tr>
<td>Kinetic energy</td>
<td>$\beta = 1$</td>
</tr>
<tr>
<td>Physical energy</td>
<td>$Ex = (h-T_0.s) - (h_0-T_0.s_0)$</td>
</tr>
<tr>
<td>Chemical energy</td>
<td>$\beta = \sim 0.8$ to 1.0, depending on composition</td>
</tr>
<tr>
<td>Heat at temperature $T$</td>
<td>$\beta = 1 - T_0/T$</td>
</tr>
<tr>
<td>Pressure of a gas</td>
<td>$Ex = n \cdot R \cdot T_0 \ln (P/P_0)$</td>
</tr>
<tr>
<td>Solar irradiation (whole spectrum)</td>
<td>$\beta = 0.9327$</td>
</tr>
<tr>
<td>Nuclear energy</td>
<td>$\beta \approx 1$</td>
</tr>
<tr>
<td>Electricity</td>
<td>$\beta = 1$</td>
</tr>
<tr>
<td>Radiation</td>
<td>$\beta = 1 + (1/3).({T_0/T}^4 - (4/3).({T_0/T})$</td>
</tr>
</tbody>
</table>
Exergy analysis for resource management:

- For a single process: exergy analysis
  - quantification of all inputs
  - quantification of all outputs
  - efficiency analysis: identification of opportunities

- For a full supply chain: cumulative exergy analysis, exergetic life cycle analysis:
  - quantification of all resources out of the environment
  - fingerprint of the extracted resources
  - overall resource efficiency of supply chain
Exergy and ELCA analysis:

- Main advantages:
  - universal
  - scientifically sound
  - one single scale for all type of energy and materials
  - allows straightforward allocation

- Main limitations:
  - Allows resource assessment rather than emissions assessment
  - Not easy to communicate
Case studies at ENVOC-UGENT
Case 1: family dwelling

- Optimization study of life cycle cost, energy consumption and pollution of a family dwelling

- Data available from Flemish study:
  - Terraced house (average Belgian dimensions)
  - 3 construction types:
    - cavity wall
    - brick wall with external insulation
    - wooden frame construction
Exergy of construction materials production (building type averages)

- Cavity wall
- External insulation
- Wooden frame

- Biomass
- Renewable energy flows (wind, …)
- Mineral aggregates
- Minerals: metal ores
- Minerals: non-metal ores
- Nuclear ores
- Organic non-renewable (oil, natural gas, …)
Annual exergy consumption

(De Meester, Dewulf et al., 2008)
Case 2: Waste gas treatment options

- **Biofiltration (BF)**
  - 3 x 700 m³
  - 50% compost (v/v); 45% polystyrene (v/v)
  - 5% CaCO₃ (v/v)

- **Activated Carbon adsorption (AC)**
  - 4 units of 7 tonnes
  - Regeneration with steam

- **Catalytic Oxidation (CO)**
  - Reactor of 15.75 m³
  - CrO₃ catalyst on Al₂O₃ support
  - Furnace gas use: 67 m³/hr

- **Thermal Oxidation (TO)**
  - 6 heat recovery units of 15 tonnes ceramics
  - Furnace gas use: 191 m³/hr
## CExC for construction and operation during 20 years (MJ)

<table>
<thead>
<tr>
<th>Material</th>
<th>CExC (MJ)</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete</td>
<td>8.93 x 10^5</td>
<td>PE</td>
</tr>
<tr>
<td>Rockwool</td>
<td>4.17 x 10^4</td>
<td>PS</td>
</tr>
<tr>
<td>Glass</td>
<td>9.01 x 10^3</td>
<td>PES</td>
</tr>
<tr>
<td>Steel</td>
<td>9.73 x 10^5</td>
<td>PUR</td>
</tr>
<tr>
<td>Steel, low alloyed</td>
<td>5.26 x 10^6</td>
<td>PVC</td>
</tr>
<tr>
<td>Steel, Zn coated</td>
<td>1.17 x 10^4</td>
<td>Alkyl paint</td>
</tr>
<tr>
<td>Reinforcement steel</td>
<td>1.38 x 10^6</td>
<td>Compost</td>
</tr>
<tr>
<td>Aluminium</td>
<td>1.25 x 10^3</td>
<td>Electricity</td>
</tr>
<tr>
<td>Zinc</td>
<td>2.18 x 10^3</td>
<td>Car transport</td>
</tr>
<tr>
<td>Copper</td>
<td>3.48 x 10^3</td>
<td>Truck (28t) transport</td>
</tr>
<tr>
<td>Limestone</td>
<td>1.71 x 10^5</td>
<td>River ship transport</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>7.10 x 10^3</td>
<td>Excavating by bulldozer</td>
</tr>
</tbody>
</table>

**TOTAL:** \(2.87 \times 10^8\) MJ
- CExC per m³ waste gas:
  - BF : 0.029 MJ
  - AC : 0.071 MJ
  - CO : 0.098 MJ
  - TO : 0.203 MJ

- Main consumption during operation
  - electricity
  - gas
  - steam
  = 83.6 to > 99.9 %

- An end-of-pipe technology (clean-up) technology is in fact now a resource management issue
- Best performance for BF mainly because operation at nearby ambient pressure and temperature
- Exergy cost ~ Economic cost

Case 3: Pharmaceuticals

In collaboration with Janssen Pharmaceutica

- Emissions are under control
- Feedstock is well known
- Resource management: fuels and feedstock
Case study: Production of Tapentadol (analgesic)

Synthesis pathway:

1. 2. 3. 4. 5.

1. $\text{CHROMATOGRAPHY}$

2. $\text{CRystallization}$

3. $\text{CHROMATOGRAPHY}$

4. $\text{Tapentadol}$
The process level = alfa system boundary

Example crystallization:
<table>
<thead>
<tr>
<th>Operations</th>
<th>Inputs</th>
<th>Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>At the reactor:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inerting</td>
<td>9.73 kg N₂ at 6 bar</td>
<td></td>
</tr>
<tr>
<td>Pumping</td>
<td>3300 kJ</td>
<td></td>
</tr>
<tr>
<td>Pumping in solution 6+7</td>
<td>1915.25 kg solution 6+7</td>
<td>9.73 kg N₂</td>
</tr>
<tr>
<td>Stirring at 80 rpm (continuous)</td>
<td>Stirring energy, 1350000 kJ</td>
<td></td>
</tr>
<tr>
<td>Heating up to 46°C</td>
<td>15740 kg Shellsol at 170°C</td>
<td>15740 kg Shellsol at 167.18°C</td>
</tr>
<tr>
<td>Pumping in HCl in 2-propanol (6N)</td>
<td>197 kg HCl solution</td>
<td>6.99 kg N₂ at 46°C</td>
</tr>
<tr>
<td>Cooling to 46°C</td>
<td>15740 kg Shellsol at -10°C</td>
<td>15740 kg Shellsol at -6.34°C</td>
</tr>
<tr>
<td>Adding seedling crystals 8</td>
<td>4.40 kg 8</td>
<td></td>
</tr>
<tr>
<td>Stirring for 7 h</td>
<td>141660 kg Shellsol at -10°C</td>
<td>141660 kg Shellsol at -9.87°C</td>
</tr>
<tr>
<td>Cooling to 40°C over 3h</td>
<td>Pumping energy, 81000 kJ</td>
<td></td>
</tr>
<tr>
<td>Cooling to 32°C over 3h</td>
<td>141660 kg Shellsol at -10°C</td>
<td>141660 kg Shellsol at -9.83°C</td>
</tr>
<tr>
<td>Cooling to 22°C over 3h</td>
<td>Pumping energy, 81000 kJ</td>
<td></td>
</tr>
<tr>
<td>Stirring for 7 h</td>
<td>141660 kg Shellsol at -10°C</td>
<td>141660 kg Shellsol at -9.79°C</td>
</tr>
<tr>
<td>Emptying reactor</td>
<td></td>
<td>2116.65 kg to filter</td>
</tr>
<tr>
<td>Cleaning reactor</td>
<td>80 kg water</td>
<td>6.74 kg N₂</td>
</tr>
<tr>
<td></td>
<td>59.25 kg MeOH</td>
<td>80 kg water</td>
</tr>
<tr>
<td></td>
<td>Pumping energy for water, 264 kJ</td>
<td>59.25 liquid MeOH at 65°C</td>
</tr>
<tr>
<td></td>
<td>Pumping energy for MeOH, 247.5 kJ</td>
<td>7083 kg Shellsol at 168.39°C</td>
</tr>
<tr>
<td></td>
<td>7083 kg Shellsol at 170°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pumping Shellsol, 4050 kJ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stirring energy, 16200 kJ</td>
<td></td>
</tr>
</tbody>
</table>
• **Efficiency:**
  - Crystallization: 7.54 %
  - Chromatography: 5.15 %

• **Exergy losses:**
Crystallization or Chromatography

Production of 6/7

Supporting processes for mass exchange
- Solvent destillation
- Solvent condensation
- Waste gas scrubbing

Supporting processes for energy exchange
- Cold shellsol production
- Hot shellsol production
- Hot water production
- Electricity delivery

Processes for energy and chemicals delivery
- Basic chemicals manufacturing
- Natural gas delivery
- Electricity delivery

Natural resources

γ system boundary (industry)

β system boundary (plant)

α system boundary (process)

6 or 8

CExC
Result gamma system boundary

- Efficiency: Crystallization: 1.25 %
  Chromatography: 1.00 %

- CExC:

(Dewulf et al., Green Chem., 2007)
Case 4: biofuels
Are biofuels the ultimate solution?

At a first glance:

Closing cycles
= reduction in resource depletion and emissions
BUT: Modern agriculture:

Pesticides & Fertilizer manufacturing

Tractors & fuels

Agricultural equipment

Combines

Maintenance & Spare parts
.. and biofuel manufacturing
RESULTS: 1 ha rapeseed:

- 10,000 GJ solar energy
- 47.5 GJ biodiesel
- Emissions (CO₂, ...)
- Electricity, Machines, Chemicals, ...
- Fossil resources 15.4 GJ
- Agricult. machinery, Pesticides, Fertilizers, ...

CO₂
Step 1: Agricultural production

- Seeds
- Nutrients
- Pesticides
- Solar input
- Fuels
- Straw
- Rapeseed

Agriculture
Step 2: Industrial biofuel production

- Rapeseed
- Transport
- Oil
- Drying, Extraction, Refining
- Steam
- Electricity
- Rape cake
- Rapeseed oil
- Methanol
- Esterification
- Glycerol
- RME
- Hexane
- Fuel
- Electric fuel
Agricultural Rapeseed Production: inputs and outputs related to 1 ha. All data are in GJ of exergy ha$^{-1}$ yr$^{-1}$.

- **Seed**: 0.19
- **Solar radiation**: 32 100
- **Pesticides**: 0.029
- **Fertilizers**: 2.62
- **Fuels**: 2.74
- **Rapeseed**: 86.0
- **Straw**: 62.1
Agricultural Rapeseed Production: inputs and outputs related to 1 ha. All data are in GJ of exergy ha$^{-1}$ yr$^{-1}$.
TABLE 1. Inputs and Outputs (GJ of Exergy) of the Conversion of the Production of 1 ha of Crops into Biofuels

<table>
<thead>
<tr>
<th></th>
<th>rapeseed</th>
<th>soybean</th>
<th>corn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>agricultural product</td>
<td>86.0</td>
<td>53.8</td>
<td>134</td>
</tr>
<tr>
<td>fuels</td>
<td>0.17</td>
<td>2.97</td>
<td>0.32</td>
</tr>
<tr>
<td>electricity</td>
<td>0.46</td>
<td>0.69</td>
<td>2.85</td>
</tr>
<tr>
<td>steam</td>
<td>1.00</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>chemicals</td>
<td>3.63</td>
<td>1.30</td>
<td>1.79</td>
</tr>
<tr>
<td>sum</td>
<td>91.3</td>
<td>59.5</td>
<td>139</td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>biofuel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RME</td>
<td></td>
<td>47.5</td>
<td></td>
</tr>
<tr>
<td>SME</td>
<td></td>
<td></td>
<td>16.4</td>
</tr>
<tr>
<td>EtOH</td>
<td></td>
<td></td>
<td>68.8</td>
</tr>
<tr>
<td>byproducts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glycerol</td>
<td>2.10</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>meal</td>
<td>32.7</td>
<td>37.3</td>
<td></td>
</tr>
<tr>
<td>DDGS</td>
<td></td>
<td></td>
<td>43.4</td>
</tr>
<tr>
<td>sum</td>
<td>82.3</td>
<td>55.0</td>
<td>112</td>
</tr>
</tbody>
</table>

Efficiency (GJ biofuel/ha) : Corn > Rapeseed > Soybean
Input of non-renewables:

Exergy (%)

Cumulative Exergy (%)

- Agricultural stage
- Drying, cleaning and storage
- Extraction and refining
- Esterification
- Transport
Overall RME production chain: inputs and outputs related to 1 ha. All data are in GJ of exergy ha\(^{-1}\) yr\(^{-1}\)

Allocation of inputs to biofuels:

Non-renewable Agricultural resources

Non-renewable Industrial resources

Agriculture

Rapeseeds

Industrial conversion

Solar Irradiation

Straw

Meal

Glycerol

RME

Inputs and outputs related to 1 ha. All data are in GJ of exergy ha\(^{-1}\) yr\(^{-1}\):
Case 5: fingerprinting energy & materials

In collaboration with
- ETH, Zurich
- eco-invent, Zurich

All natural resources (>100 types): grouped into 8 categories for fingerprinting
Fingerprinting energy resources

(Dewulf et al., Environ. Sci. Technol., 2007)
Fingerprinting materials

(Dewulf et al., Environ. Sci. Technol., 2007)
Ongoing projects

- EU projects: Prosuite (FP 7), Eco²Chem (EFRD)
- FWO: forest ecosystems
- VLIR: anaerobic digestion in Cuba & Kenya
- IWT: precious metal industry, pharma industry
- MSc theses with biorefineries, ...
- ...
- ...
Conclusions

Good resource management will become more and more a central theme in developing sustainable technology.

Good resource management is aided by quantitative tools that need:
- Overall chain consideration (system boundaries)
- Proper allocation of resources to respective products
- A proper (single) quantification unit
Exergy analysis meets these needs, allowing:
- overall/integrated resource intake assessment
- proper assessment of both energy and materials

But also offers opportunities for
- overall/integrated efficiency assessment
- helps quantifying environmental sustainability: LCA & ELCA