Manufacturing, Renewable Energy and Thermodynamics

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Outline

1. The role of mfg in renewable energy
2. Thermodynamic analysis of mfg process
3. How to improve mfg processes
4. How to improve renewable energy
Role in “New Energy”
Energy Payback

Time to breakeven =
\[ t_B = \frac{E_m}{e} \]

Energy Return on Energy Investment =
\[ EROI = \frac{e t_L}{E_m} \]
Efficiencies of Energy Production, “e”

$$\eta = \frac{\text{energy out}}{\text{energy in}}$$

$$\eta_{\text{Carnot}} = \frac{\text{work out}}{\text{heat in}} = (1 - \frac{T_L}{T_H})$$
Efficiencies of Energy Production, Photovoltaic

$$\eta_{PV} = \frac{e_{out}}{e_{avail}}$$

$$e_{out} = \eta_{PV} e_{avail}$$

$\eta_{PV}$

PV: Shockley - Queisser Limit
For a simple single junction Device depends on band-gap $\sim 30\%$
Efficiencies of Energy Production, Wind

\[ \eta_{\text{Wind}} = \frac{e_{\text{out}}}{e_{\text{avail}}} \]

\[ e_{\text{out}} = \eta_{\text{Wind}} e_{\text{avail}} \]

Wind: Betz Limit \(~\approx 59\%\)
Efficiencies of Energy Production, Nuclear Power

\[ \eta = \frac{\text{energy out}}{\text{energy in}} \]

\[ \eta_{\text{Carnot}} = \frac{\text{work out}}{\text{heat in}} = \left(1 - \frac{T_L}{T_H}\right) \]

\( \eta_{\text{Carnot}} \)
Nuclear: Carnot Limit
Efficiencies of Mfg Energy Requirement, “$E_m$”

$$\eta_{mfg} = \frac{E_{\text{output}}}{E_{\text{in}}}$$

How to calculate the thermodynamic efficiency of a materials transformation process?
The minimum work to transform materials =

change in available energy or “exergy” (B) of the materials

\[ W_{\text{min}} = B_{\text{out}} - B_{\text{in}} \]
Efficiencies of Mfg Exergy Requirement, “$B_{in}$”

$$\eta_{mfg} = \frac{B_{output}}{B_{in}} = \eta_P$$

$$B_{in} = \frac{B_{output}}{\eta_P}$$

$$\eta_P = ?$$
Rewriting...

\[
\begin{align*}
    t_B &= \frac{E_{mfg}}{e} \approx \frac{\text{Exergy inputs for mfg}}{\text{Exergy output}} \\
    t_B &= \frac{B_{in}}{e_{out}} = \frac{B_{out}}{\eta_P \eta_e e_{available}}
\end{align*}
\]

\[
EROI = \frac{e t_L}{E_{mfg}} \approx \frac{e_{available} \eta_P \eta_e t_L}{B_{out}}
\]
## Current Estimates*

<table>
<thead>
<tr>
<th>Time to break even</th>
<th>EROI**</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Wind ~ 1 year</td>
<td>• Wind ~ 25</td>
</tr>
<tr>
<td>• Nuclear ~2-5 years</td>
<td>• Nuclear ~ 10 to 30</td>
</tr>
<tr>
<td>• PV ~ 2 to 5 years</td>
<td>• PV ~ 5 to 12</td>
</tr>
</tbody>
</table>

*Values can range considerably, these agree with Smil 2008  
**Using $T_L$ of 25 yrs for PV and Wind, and 50 yrs for Nuclear.  
NOTE: PV and Wind do not include storage
Thermodynamic Analysis of Resources Used in Manufacturing Processes
Energy Conversion

Materials Production

Auxiliary Materials Production

Energy Conversion

Aux. Mfg Process Equipment

Energy Conversion

Mfg Process Equipment

Energy Conversion

Mfg Process Equipment

Environmental Conditioning
Hybrid Input Output Analysis
(transportation, capital equipment, other materials, commercial buildings...)

Diagram showing the flow of energy conversion, production, and conditioning processes.
Thermodynamic Analysis: Materials Transformation, Open System

\[ \dot{m}_a, \dot{H}_a, \dot{S}_a \rightarrow \quad \rightarrow \dot{m}_b, \dot{H}_b, \dot{S}_b \]

\[ \dot{W}, \dot{Q} \quad (T_0, p_0) \]
Balance Equations

\[ \frac{dM}{dt} = \dot{m}_a - \dot{m}_b = 0, \quad (\dot{m}_a = \dot{m}_b = \dot{m}) \quad \text{steady state} \]

\[ \frac{dE}{dt} = \dot{H}_a + \dot{W} - \dot{Q} - \dot{H}_b = 0 \quad \text{steady state} \]

\[ \frac{dS}{dt} = \dot{S}_a - \frac{\dot{Q}}{T_0} - \dot{S}_b + \dot{S}_{\text{irr}} = 0 \quad \text{steady state} \]
Eliminating $\dot{Q}$, gives Work Rate

$$\dot{W} = H_b - H_a - T_o (\dot{S}_b - \dot{S}_a) + T_o \dot{S}_{\text{irr}}$$

$$= \dot{H}_b - T_o \dot{S}_b - (\dot{H}_a - T_o \dot{S}_a) + T_o \dot{S}_{\text{irr}}$$

$$+ (\dot{H}_o - T_o \dot{S}_o) - (\dot{H}_o - T_o \dot{S}_o)$$

$$\dot{W} = \dot{B}_b - \dot{B}_a + T_o \dot{S}_{\text{irr}}$$
In terms of Minimum Work

\[ \dot{W} = \dot{B}_b - \dot{B}_a + T_0 \dot{S}_{\text{irr}} \]

For the ideal case "reversible process"

\[ (T_0 \dot{S}_{\text{irr}} = 0) \quad w_{\text{min}} = \frac{\dot{W}}{\dot{m}} = b_b - b_a \]

intensive form, exergy per mole or mass, or

extensive form \[ W_{\text{min}} = B_b - B_a \]
Chemical Properties referenced to the “environment”

\[ T_0 = 298.2 \text{ K}, \quad P_0 = 101.3 \text{ kPA} \]
Exergy Reference System

- pure metal, element
- oxides, sulfides...
- crustal component
  earth’s crust (ground state)

{ chemical reactions

{ extraction
Exergy Reference System

Aluminum (c=1) 888.4 kJ/mole

$\text{Al}_2\text{O}_3$ (c=1) 200.4 kJ/mole

$\text{Al}_2\text{SiO}_5$ (c=1) 15.4 kJ/mole

$\text{Al}_2\text{SiO}_5$ (c = $2 \times 10^{-3}$) 0 kJ/mole (ground)
Example: making pure iron from the crust

Fe (c = 1) \[ \rightarrow \] \[376.4 \text{ kJ/mole}\]

Fe\(_2\)O\(_3\) (c = 1) \[ \rightarrow \] \[16.5 \text{ kJ/mole}\]

Fe\(_2\)O\(_3\) (c = 1.3 \times 10^{-3}) \[ \rightarrow \] \[0 \text{ kJ/mole (ground)}\]
Table 2.8 Solid reference species and their conventional average concentration in the external layer of the earth crust

<table>
<thead>
<tr>
<th>Chemical element</th>
<th>Component of the lithosphere</th>
<th>Reference species</th>
<th>Conventional standard mole fraction ( x_m )</th>
<th>Standard chemical exergy, ( \text{kJ/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (s)</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>( \text{Al}_2\text{SiO}_3 ) (sillimanite)</td>
<td>( 2 \times 10^{-3} )</td>
<td>15.4</td>
</tr>
<tr>
<td>Ba</td>
<td>( \text{BaO} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>( \text{CaO} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>( \text{Cl} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co (s)</td>
<td>( \text{Co} )</td>
<td>( \text{Co}_2\text{O}_4 )</td>
<td>( 2 \times 10^{-7} )</td>
<td>38.2</td>
</tr>
<tr>
<td>Cr (s)</td>
<td>( \text{Cr}_2\text{O}_3 )</td>
<td>( \text{Cr}_2\text{O}_3 ) (s)</td>
<td>( 4 \times 10^{-7} )</td>
<td>36.5</td>
</tr>
<tr>
<td>Fe (s)</td>
<td>( \text{Fe} )</td>
<td>( \text{Fe}_2\text{O}_3 ) (s)</td>
<td>( 1.3 \times 10^{-3} )</td>
<td>16.5</td>
</tr>
<tr>
<td>K</td>
<td>( \text{K}_2\text{O} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mg (s)</td>
<td>( \text{MgO} )</td>
<td>( \text{CaCO}_3 \cdot \text{MgCO}_3 )</td>
<td>( 2.3 \times 10^{-3} )</td>
<td>15.1</td>
</tr>
<tr>
<td>Mn (s)</td>
<td>( \text{MnO} )</td>
<td>( \text{MnO}_2 )</td>
<td>( 2 \times 10^{-4} )</td>
<td>21.1</td>
</tr>
<tr>
<td>Na</td>
<td>( \text{Na}_2\text{O} )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P (s)</td>
<td>( \text{P}_2\text{O}_5 )</td>
<td>( \text{Ca}_3(\text{PO}_4)_2 )</td>
<td>( 4 \times 10^{-4} )</td>
<td>19.4</td>
</tr>
<tr>
<td>S</td>
<td>( \text{SO}_3 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sb (s), III</td>
<td>Sb</td>
<td>( \text{Sb}_2\text{O}_3 )</td>
<td>( 7 \times 10^{-10} )</td>
<td>52.3</td>
</tr>
<tr>
<td>Si (s)</td>
<td>( \text{SiO}_2 )</td>
<td>( \text{SiO}_2 ) (s)</td>
<td>0.472</td>
<td>1.9</td>
</tr>
<tr>
<td>Sn (s), white</td>
<td>Sn</td>
<td>( \text{SnO}_2 ) (s)</td>
<td>( 8 \times 10^{-6} )</td>
<td>29.1</td>
</tr>
<tr>
<td>Ti (s), II</td>
<td>TiO(_2)</td>
<td>TiO(_2) (s), III</td>
<td>( 1.8 \times 10^{-4} )</td>
<td>21.4</td>
</tr>
<tr>
<td>U (s), III</td>
<td>U</td>
<td>UO(_3) (s)</td>
<td>( 2 \times 10^{-8} )</td>
<td>43.9</td>
</tr>
<tr>
<td>V (s)</td>
<td>V(_2)O(_5)</td>
<td>V(_2)O(_5) (s)</td>
<td>( 2 \times 10^{-6} )</td>
<td>32.5</td>
</tr>
</tbody>
</table>
Extraction from the crust

Extracting Fe\textsubscript{2}O\textsubscript{3} from c = 1.3x10\textsuperscript{-3} (crust) to c = 1

\[
B = T_o R \ln \frac{1}{1.3 \times 10^{-3}}
\]

\[
B = 298.2^\circ K \times 8.314 \frac{J}{\text{mole}^\circ K} \times \ln \frac{1}{1.3 \times 10^{-3}} = 16.5 \frac{kJ}{\text{mole}}
\]

Note: R = k N\textsubscript{avo} (Boltzmann’s constant X Avogadro’s number)
Reduction of Fe$_2$O$_3$ (Hematite)

\[2\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Fe} + 3\text{CO}_2\]

Output = $4 \times 376.4 - 3 \times 19.9$

- Input = $-(2 \times 16.5 + 3 \times 410.3)$

\[W_{min} = 301.4 \text{ kJ}\]
Actual exergy expenditure = \( \sum B_{inputs} \)

\[ W = B_b - B_a + T_0 S_{irr} \]

\[ \eta_P = \frac{B_{product}}{\sum B_{inputs}} \]

\[ B_{product} \leq B_b \]
Iron Ore Reduction

the actual reaction is

\[ 2\text{Fe}_2\text{O}_3 + 12.42\text{C} + 9.42\text{O}_2 \rightarrow 4\text{Fe} + 12.42\text{CO}_2 \]

\[ 33\text{kJ} + 5095.9 + 37.7 - 1505.6 - 247.2 \text{kJ} = \]

actual work = 3,413.8 kJ for 4 mole of Fe

\[ \eta_P = \frac{1505.6}{5166.6} = 0.29 \]
Manufacturing Systems

Manufacturing Systems as open thermodynamic systems

Gutowski et al. ES&T 2009
Balances for Mfg Process

Mass
\[
\frac{dm_{MF}}{dt} = \left( \sum_{i=1}^{\text{in}} \dot{N}_{i,in} M_i \right)_{MF} - \left( \sum_{i=1}^{\text{out}} \dot{N}_{i,out} M_i \right)_{MF}
\]

Energy
\[
\frac{dE_{MF}}{dt} = \sum_{i} \dot{Q}_{ECMF}^{MF} - \dot{Q}_{0}^{MF} + \dot{W}_{ECMF}^{MF} + \dot{H}_{MF}^{mat} - \dot{H}_{MF}^{prod} - \dot{H}_{MF}^{res}
\]

Entropy
\[
\frac{dS_{MF}}{dt} = \sum_{i} \frac{\dot{Q}_{ECMF}^{MF}}{T_i} - \frac{\dot{Q}_{0}^{MF}}{T_0} + \dot{S}_{MF}^{mat} - \dot{S}_{MF}^{prod} - \dot{S}_{MF}^{res} + \dot{S}_{irr,MF}
\]
Work Rate for Mfg Process in Steady State

\[
\begin{align*}
\dot{W}_{ECMF}^{MF} &= ((\dot{H}_{MF}^{prod} + \dot{H}_{MF}^{res}) - \dot{H}_{MF}^{mat}) \\
&- T_0 ((\dot{S}_{MF}^{prod} + \dot{S}_{MF}^{res}) - \dot{S}_{MF}^{mat}) \\
&- \sum_{i>0} \left(1 - \frac{T_0}{T_i}\right) Q_{ECMF}^{MF} + T_0 \dot{S}_{irr,MF}
\end{align*}
\]
**Exergy and Work**

\[ B = (H - T_o S) - (H - T_o S)_o \]

\[
\dot{W}_{ECMF \leftarrow MF} = ((\dot{B}_{MF}^{prod} + \dot{B}_{MF}^{res}) - \dot{B}_{MF}^{mat}) \\
- \sum_{i>0} \left(1 - \frac{T_0}{T_i}\right) \dot{Q}_{ECMF \leftarrow MF} + T_0 \dot{S}_{irr, MF}
\]

Examples: plastic work, melting, vaporizing etc.
Physical & Chemical Exergy

\[
\dot{W}_{ECMF}^{MF} = \left( (\dot{B}_{MF}^{\text{prod}} + \dot{B}_{MF}^{\text{res}}) - \dot{B}_{MF}^{\text{mat}} \right)^{ph} \\
+ \left( \sum_{i=1}^{n} b_{i}^{ch} \dot{N}_{i} \right)^{\text{prod}}_{MF} + \left( \sum_{i=1}^{n} b_{i}^{ch} \dot{N}_{i} \right)^{\text{res}}_{MF} - \\
\left( \sum_{i=1}^{n} b_{i}^{ch} \dot{N}_{i} \right)^{\text{mat}}_{MF} - \sum_{i>0} \left( 1 - \frac{T_{0}}{T_{i}} \right) \dot{Q}_{ECMF}^{MF} + T_{0} \dot{S}_{irr,MF}
\]

Here all chemical exergy terms \((b^{ch})\) are at \(T_{o}, P_{o}\)

Branham et al IEEE ISEE 2008
Example Calculations
Second Law Efficiency; Degree of Perfection

- Induction melting or iron
- PECVD of SiO2
- Thermal Oxidation of SiO2

\[ \eta_p = \frac{B_{\text{useful output}}}{B_{\text{in}}} \]
Induction Melting Exergy Analysis

Boundaries are drawn around the entire facility, all components are at standard pressure and temperature.
# Batch Induction Melter Exergy Analysis*

## Ductile Iron Batch Electric Induction Melting

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (kg)</th>
<th>Weight Percent</th>
<th>Standard Chemical Exergy (MJ/kg)</th>
<th>Exergy (MJ)</th>
<th>Percent Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input Materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel Scrap</td>
<td>439</td>
<td>42.85%</td>
<td>6.89</td>
<td>3022.25</td>
<td>15.39%</td>
</tr>
<tr>
<td>Pig Iron</td>
<td>1.6</td>
<td>0.16%</td>
<td>8.18</td>
<td>13.43</td>
<td>0.07%</td>
</tr>
<tr>
<td>Ductile Iron Remelt</td>
<td>535</td>
<td>52.25%</td>
<td>8.44</td>
<td>4513.98</td>
<td>22.99%</td>
</tr>
<tr>
<td>65% Silicon Carbide Briquettes</td>
<td>4.3</td>
<td>0.42%</td>
<td>31.73</td>
<td>137.62</td>
<td>0.70%</td>
</tr>
<tr>
<td>75% Ferrosilicon</td>
<td>3.0</td>
<td>0.29%</td>
<td>24.51</td>
<td>72.46</td>
<td>0.37%</td>
</tr>
<tr>
<td>5% MgFeSi</td>
<td>14.8</td>
<td>1.44%</td>
<td>19.09</td>
<td>282.30</td>
<td>1.44%</td>
</tr>
<tr>
<td>Copper</td>
<td>1.7</td>
<td>0.17%</td>
<td>2.11</td>
<td>3.69</td>
<td>0.02%</td>
</tr>
<tr>
<td>Tin</td>
<td>0.005</td>
<td>0.00%</td>
<td>1.13</td>
<td>0.01</td>
<td>0.00%</td>
</tr>
<tr>
<td>62% Fe-Molybdenum</td>
<td>6.2</td>
<td>0.61%</td>
<td>7.28</td>
<td>45.35</td>
<td>0.23%</td>
</tr>
<tr>
<td>Carbon 9012</td>
<td>18</td>
<td>1.80%</td>
<td>34.16</td>
<td>628.45</td>
<td>3.20%</td>
</tr>
<tr>
<td>Natural Gas Preheater</td>
<td>0.02</td>
<td>0.00%</td>
<td>51.84</td>
<td>1.27</td>
<td>0.01%</td>
</tr>
<tr>
<td>Electricity</td>
<td></td>
<td></td>
<td></td>
<td>5418.00</td>
<td>55.59%</td>
</tr>
<tr>
<td><strong>Total Inputs</strong></td>
<td>1024</td>
<td>100.00%</td>
<td></td>
<td>14138.83</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

| **Output Materials**              |             |                |                                  |             |               |
| Ductile Iron Melt                 | 1000.2      | 96.69%         | 8.44                             | 8436.45     | 99.29%        |
| Slag                              | 33.9        | 3.28%          | 1.14                             | 60.05       | 0.71%         |
| Dust                              | 0.3         | 0.02%          | 0.26                             | 0.07        | 0.00%         |
| **Total Outputs**                 | 1034        | 100.00%        |                                  | 8497        | 100.00%       |

**Mass Difference**                | -1.05%      |                |                                  |             |               |

*including losses at Utility
Batch Electric Degree of Perfection

\[ \eta_p = \frac{\text{Exergy of useful products}}{\text{Exergy of inputs}} \]

Total Exergy In (Bin) = 11,155,000 J

Batch Electric Induction Melting
of 1 kg of melt

Useful Exergy Out (Bout) = 8,250,000 J

<table>
<thead>
<tr>
<th>Component</th>
<th>Exergy in (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallics</td>
<td>8,700,000</td>
</tr>
<tr>
<td>Electricity*</td>
<td>2,455,000</td>
</tr>
</tbody>
</table>

*not including utility losses

Degree of Perfection

\[ \eta_p = \frac{8,250,000 J}{10,420,000 J} = 0.79 \]
Plasma Enhanced Chemical Vapor Deposition (CVD)

$\text{SiH}_4 \text{(gas)} + 2\text{N}_2\text{O \text{(gas)}} \rightarrow \text{SiO}_2\text{(solid)} + 2\text{N}_2\text{(gas)} \ 2\text{H}_2 \text{(gas)}$
## Input Deposition Gases

<table>
<thead>
<tr>
<th>Species</th>
<th>Input mass (g)</th>
<th>Input moles or primary energy</th>
<th>Exergy (J)</th>
<th>%Total Inputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH4</td>
<td>0.95</td>
<td>0.029579mol</td>
<td>40928.6</td>
<td>0.749</td>
</tr>
<tr>
<td>O2</td>
<td>0.49</td>
<td>0.015313mol</td>
<td>60.79</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>0.34</td>
<td>0.008511mol</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>196.9</td>
<td>7.028779mol</td>
<td>4849.9</td>
<td></td>
</tr>
</tbody>
</table>

## Input Cleaning Gases

<table>
<thead>
<tr>
<th>Species</th>
<th>Input mass (g)</th>
<th>Input moles or primary energy</th>
<th>Exergy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>69.41</td>
<td>4.326643mol</td>
<td>3598253</td>
</tr>
<tr>
<td>NF3</td>
<td>31.06</td>
<td>0.437453mol</td>
<td>266931.6</td>
</tr>
</tbody>
</table>

## Input Energy

<table>
<thead>
<tr>
<th>Energy</th>
<th>Input</th>
<th>Exergy (J)</th>
<th>%Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td>2220000J</td>
<td>2220000</td>
<td>36.2</td>
</tr>
</tbody>
</table>

## Outputs

<table>
<thead>
<tr>
<th>Outputs</th>
<th>Input mass or primary energy</th>
<th>Exergy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Silicate Glass laye</td>
<td>0.0248</td>
<td>3.2667</td>
</tr>
</tbody>
</table>
**CVD Degree of Perfection**

Total Exergy In (Bin) = 6,130,000 J

Chemical Vapor Deposition (CVD) of a 600nm Undoped Silicate Glass (USG) layer at 400°C

Useful Exergy Out (Bout) = 3.3 J

<table>
<thead>
<tr>
<th>Component</th>
<th>Exergy in (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Gases</td>
<td>45,900</td>
</tr>
<tr>
<td>Cleaning Gases</td>
<td>3,865,000</td>
</tr>
<tr>
<td>Electricity*</td>
<td>2,220,000</td>
</tr>
</tbody>
</table>

*not including utility losses

Degree of Perfection

$$\eta_p = \frac{3.267 J}{6,131,123 J} = 5.33 \times 10^{-7}$$

Data from Sarah Boyd et. al. (2006)
Thermal (Wet) Oxidation

\[
Si \text{ (solid)} + H_2O \text{ (vapor)} \rightarrow SiO_2 \text{ (solid)} + 2H_2 \text{ (gas)}
\]
### Input Gases

<table>
<thead>
<tr>
<th>Species</th>
<th>Input mass (g)</th>
<th>Input moles or energy (J)</th>
<th>Exergy (J)</th>
<th>%Total Input Exergy</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>54.069</td>
<td>1.9301</td>
<td>1331.769</td>
<td>0.00089</td>
</tr>
<tr>
<td>O2</td>
<td>6.1399</td>
<td>0.19188</td>
<td>761.7636</td>
<td>0.00051</td>
</tr>
<tr>
<td>H2</td>
<td>0.4479</td>
<td>0.22218</td>
<td>52456.7</td>
<td>0.0351</td>
</tr>
</tbody>
</table>

### Silicon Consumed from Substrate

| Si      | 0.03091        | 0.001101                  | 940.54     | 0.00063              |

### Input Energy

| Electricity | 149256000 | 149256000 | 0.99963 |

### Outputs

| SiO2 layer | 0.066253 | 0.001103 | 8.711   |

**degree of perfection**

\[ n_P = 5.83 \times 10^{-8} \]
Summary for $\eta_P$

- Heating & Melting $\sim 0.5$
- Machining $\sim 0.05$
- Grinding $\sim 0.005$
- Sputter, Wet and Dry Etching $\sim 5 \times 10^{-4}$
- PECVD (SiO2) $\sim 10^{-6}$
- Wet Oxidation $\sim 10^{-8}$
Comments

• These can be quite sensitive to rate when idle power is high
• Transit Exergy for melting processes
• Exergy of Auxiliary materials: etching, cleaning, pollution abatement, abrasive waterjet
• Also affected by exergy of the output
**Energy (Electricity) Only**

1. Machining
2. Grinding
3. Casting
4. Injection Molding
5. Abrasive Waterjet
6. EDM
7. Laser DMD
8. CVD
9. Sputtering
10. Thermal Oxidation
Energy Requirements at the Machine Tool

Energy Use Breakdown by Type

Production Machining Center

Automated Milling Machine

Electric Energy Intensity for Manufacturing Processes

\[ P = P_0 + k_v \dot{V}_{\text{processed}} \]

\[ \frac{P}{\dot{V}} = \frac{P_0}{\dot{V}} + k_v = \frac{E}{V} \]
**Injection Molding Machines**

Does not account for the electric grid.

\[
\frac{P}{m} = \frac{P_o}{\dot{m}} + k_m = \frac{E}{m}
\]
Thermal Oxidation, $SiO_{2\Delta}$

![Graph showing energy consumption for growth of a 25-Å oxide layer as a function of equipment type (RTP vs vertical furnace), number of wafers processed per week, and total run time (production plus idle). The example shown is for 8-in. wafers.]

Ref: Murphy et al \(\text{es&t 2003}\)
### Power Requirements

#### TABLE 2. Average Number of Functions, Throughputs, and Power Requirements for a Hypothetical 0.13-μM Microprocessor Wafer Fab

<table>
<thead>
<tr>
<th>unit operation</th>
<th>no. of functions</th>
<th></th>
<th></th>
<th></th>
<th>power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8-layer metal</td>
<td>6-layer metal</td>
<td>wafers/ run</td>
<td>wafers/ h</td>
<td>process</td>
</tr>
<tr>
<td>implant</td>
<td>16</td>
<td>16</td>
<td>25</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>CVD</td>
<td>13</td>
<td>11</td>
<td>10</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>wafer clean</td>
<td>35</td>
<td>31</td>
<td>50</td>
<td>150</td>
<td>8</td>
</tr>
<tr>
<td>furnace</td>
<td>21</td>
<td>17</td>
<td>150</td>
<td>35</td>
<td>21</td>
</tr>
<tr>
<td>furnace (RTP)</td>
<td>7</td>
<td>7</td>
<td>1</td>
<td>10</td>
<td>48</td>
</tr>
<tr>
<td>photo (stepper)</td>
<td>27</td>
<td>23</td>
<td>1</td>
<td>60</td>
<td>115</td>
</tr>
<tr>
<td>photo (coater)</td>
<td>27</td>
<td>23</td>
<td>1</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>etch (pattern)</td>
<td>24</td>
<td>20</td>
<td>1</td>
<td>35</td>
<td>135</td>
</tr>
<tr>
<td>etch (ash)</td>
<td>27</td>
<td>23</td>
<td>1</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>metallization</td>
<td>11</td>
<td>9</td>
<td>1</td>
<td>25</td>
<td>150</td>
</tr>
<tr>
<td>CMP</td>
<td>18</td>
<td>14</td>
<td>1</td>
<td>25</td>
<td>29</td>
</tr>
</tbody>
</table>

Ref: Murphy et al. es&t 2003
<table>
<thead>
<tr>
<th>Process Name</th>
<th>Power Required</th>
<th>Process Rate</th>
<th>Electricity Required</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kW</td>
<td>cm³/s</td>
<td>J/cm³</td>
<td></td>
</tr>
<tr>
<td>Injection Molding</td>
<td>10.76 - 71.40</td>
<td>3.76 - 50.45</td>
<td>1.75E+03 - 3.41E+03</td>
<td>[Thiriez 2006]</td>
</tr>
<tr>
<td>Machining</td>
<td>2.80 - 194.80</td>
<td>0.35 - 20.00</td>
<td>3.50E+03 - 1.87E+05</td>
<td>[Dahmus 2004], [Morrow, Qi &amp; Skerlos 2004] &amp; [Time Estimation Booklet 1996]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>5.04 - 19.50</td>
<td>1.05E-05 - 6.70E-04</td>
<td>7.52E+06 - 6.45E+08</td>
<td>[Wolf &amp; Tauber 1986] &amp; [Holland Interview]</td>
</tr>
<tr>
<td>Grinding</td>
<td>7.50 - 0.03</td>
<td>1.66E-02 - 2.85E-02</td>
<td>6.92E+04 - 3.08E+05</td>
<td>[Baniszewski 2005] &amp; [Chryssolouris 1991]</td>
</tr>
<tr>
<td>Waterjet</td>
<td>8.16 - 16.00</td>
<td>5.15E-03 - 8.01E-02</td>
<td>2.06E+05 - 3.66E+06</td>
<td>[Kurd 2004]</td>
</tr>
<tr>
<td>Wire EDM</td>
<td>6.60 - 14.25</td>
<td>2.23E-03 - 2.71E-03</td>
<td>2.44E+06 - 6.39E+06</td>
<td>[Sodick], [Kalpakjian &amp; Schmid 2001], &amp; [AccuteX 2005]</td>
</tr>
<tr>
<td>Drill EDM</td>
<td>2.63</td>
<td>1.70E-07</td>
<td>1.54E+10</td>
<td>[King Edm 2005] &amp; [McGeough, J.A. 1988]</td>
</tr>
<tr>
<td>Laser DMD</td>
<td>80.00</td>
<td>1.28E-03</td>
<td>6.24E+07</td>
<td>[Morrow, Qi &amp; Skerlos 2004]</td>
</tr>
<tr>
<td>Thermal Oxidation</td>
<td>21.00 - 48.00</td>
<td>4.36E-07 - 8.18E-07</td>
<td>2.57E+10 - 1.10E+11</td>
<td>[Murphy et al. 2003]</td>
</tr>
</tbody>
</table>
In General, over many manufacturing processes,

Idle Power

\[ 5kW \leq P_o \leq 50kW \]

and

Material Process Rates

\[ 10^{-7} \text{ cm}^3/\text{sec} \leq \dot{V} \leq 1 \text{ cm}^3/\text{sec} \]
Specific Energy Requirements J/cm³ for Various Mfg Processes

Electricity Requirements [J/cm³]

Process Rate [cm³/s]

- Injection Molding
- Machining
- Finish Machining
- CVD
- Sputtering
- Grinding
- Abrasive Waterjet
- Wire EDM
- Drill EDM
- Laser DMD
- Oxidation

Lower Bound

Upper Bound

Gutowski et al
IEEE, ISEE 2007
Specific Energy Requirements $J/cm^3$ for Various Mfg Processes

Advanced Processes & Mico/Nano

Conventional Processes

Gutowski et al.
IEEE, ISEE 2007

8 orders of magnitude

Electricity Requirements $[J/cm^3]$ vs. Process Rate $[cm^3/s]$
Electricity Requirements [J/kg]

Process Rate [kg/hr]

- Injection Molding
- CVD
- Abrasive Waterjet
- Wire EDM
- Laser DMD

Gutowski et al. IEEE, ISEE 2007
Electricity Requirements [J/kg] vs. Process Rate [kg/hr]
Why are these energy intensities so high?

- demand for small devices, prices for energy & materials stable/declining
- vapor phase processes with slow deposition rates
- efficiency used to enhance performance, not to downsize equipment
- However, the trajectory of individual processes is usually toward faster rates and lower energy intensities
Keep in Mind

- This is intensity not total used
- This is at the process, not cumulative exergy!
  - loses at energy conversion not included
  - investment into materials not included
  - infrastructure not included
How to Improve mfg processes
Mostly Vapor Phase Processes

Melting & Machining

Electricity Requirements [J/kg]

Process Rate [kg/hr]

- Injection Molding [20]
- CVD [5, 29, 34]
- Abrasive Waterjet [23]
- Laser DMD [33]
- Cupola Melter [26]
- PECVD of a Nitride Film [28]
- Sputtering of AlCu [28]
- Machining [18]
- Sputtering [29, 34]
- Wire EDM [29, 32]
- Oxidation [6]
- Grinding [22]
- Drill EDM [29, 35]
- Melters [28]
- PECVD of an Oxide Film [28]
- Dry Etching of a Nitride Film [28]
- Carbon Nanotube Production [28]
**FIGURE 22.6** Relative time required to machine with various cutting-tool materials, indicating the year the tool materials were first introduced. Note that machining time has been reduced by two orders of magnitude within a hundred years. *Source:* Courtesy of Sandvik.
Turn un-needed equipment off!

![Graph showing SEC (MJ/kg) vs. Throughput (kg/hr) for All-Electric and Hydraulic 85 tons equipment. Material: PP. Source: Thiriez 2006]
Analog Devices MPD Fab Power Consumption Distribution (kW)

- DI Water: 133.4 kW (9%)
- Air Handling/Circulation: 135.2 kW (9%)
- Air Compression: 98.0 kW (7%)
- Chilling/Air Conditioning: 415.4 kW (28%)
- Scrubber System: 44.4 kW (3%)
- Fab Tools: 612.3 kW (43%)
- Other: 18.811 kW (1%)

Total = 1457.4 kW

Figure 4.14: Electricity Use Breakdown of the Analog Devices MPD Wafer Fab (Excludes Lighting, non-Fab-Related Air Handling)
Use Less Materials

In ID and wire sawing of Si ingots, the kerf material represents lost exergy.

String-Ribbon
Invented by Ely Sachs
saves this material
Change Basic Mechanism

Xerox goes from grinding to emulsion polymerization
To produce toner particles
Returning to renewable energy

\[ t_B = \frac{E_{mfg}}{e} \approx \frac{\text{Exergy inputs for mfg}}{\text{Exergy output}} \]

\[ t_B = \frac{B_{in}}{e_{out}} = \frac{B_{out}}{\eta_P \eta_e e_{available}} \]

\[ \text{EROI} = \frac{et_L}{E_{mfg}} \approx \frac{e_{available} \eta_P \eta_e t_L}{B_{out}} \]
Summary Comments

• Manufacturing processes can be treated as thermodynamic processes

• They play an important role in renewable energy
Thank You

gutowski@mit.edu
Google: Environmentally Benign Manufacturing

Ref paper:

Gutowski, Branham, Dahmus, Jones, Thiriez and Sekulic