Techno-Economic Modeling of Algal Processes with Aspen

Some Lessons Learned

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Lesson Learned 1: M&EB

- A fully converged mass and energy balance for the total SYSTEM is essential.

- Without it, a model has limited use.

- It can be started on a spreadsheet, but cannot finish there.
Lesson Learned 2: Choice of Simulator

- Process simulation is essential.

- Using a full process simulator such as Aspen Plus is a good investment in money and time, but it is not enough.

- A range of simulators is available (see next slide) but we found that AspenPlus and Comsol worked best for us.
## Lesson Learned 2: Choice of Simulator

<table>
<thead>
<tr>
<th>EXTERNAL</th>
<th>INTERNAL</th>
<th>OPTIONAL LINKS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspen Simulation Workbook (optional)</td>
<td>[</td>
<td>ansys Fluent</td>
</tr>
<tr>
<td>MS Excel</td>
<td>[</td>
<td>comsol Multiphysics</td>
</tr>
<tr>
<td>Data checking &amp; analysis</td>
<td>[</td>
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</tr>
<tr>
<td>Making accessible to non-Aspen users</td>
<td>[</td>
<td>reactor design &amp; DEPTH</td>
</tr>
<tr>
<td>Transfer to outside world</td>
<td>[</td>
<td>light penetration</td>
</tr>
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<td></td>
<td>[</td>
<td>monod kinetics</td>
</tr>
<tr>
<td></td>
<td>[</td>
<td>photoinhibition</td>
</tr>
<tr>
<td></td>
<td>[</td>
<td>coupling reaction kinetics with turbulence (k-ε)</td>
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<tr>
<td></td>
<td></td>
<td>comsol Reaction Engineering Lab</td>
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<tr>
<td></td>
<td></td>
<td>flow3D</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3D dynamic simulations</td>
</tr>
<tr>
<td></td>
<td></td>
<td>evaporation</td>
</tr>
</tbody>
</table>

### Other Optional links
- **Oracle Project (Primavera) (or MS Project)**
  - Project Management
- **Crystal Ball or @Risk**
  - Monte Carlo and Sensitivity Analysis

**ASPNPLUS® as backbone to Integrated Systems Process Model for Design, Development, Costing and Analysis**
Lesson Learned 3: Reactive vs Proactive Simulation

**“NORMAL” ASPEN+ OPERATION**
- Excellent when the process has been decided.
- As needs a lot of information to be supplied.
- Great for a mature process. Unable to make predictions about an immature process.

**INPUT STREAMS DEFINED**
- REACTOR CONFIGURATION DEFINED
- Provide:
  - Pond areas
  - Oil Production
  - Cell density at harvesting
  - Reaction kinetics etc etc

**OUTPUT STREAMS PREDICTED**
- GOOD FOR DEALING WITH THE PAST

**“REVERSE” ASPEN+ OPERATION**
- i.e. tell Aspen what you want and let it tell you how to get it.
- Typically solves 50,000 simultaneous equations (and their derivatives)
- so if what you ask for is unreasonable it will never converge.

**INPUT STREAMS DEFINED**
- REACTOR CONFIGURATION PREDICTED
- Pond Areas predicted
- Productivities predicted
- Oil content of cell predicted
- Identifies opportunities for improvement
- Takes a lot of setting up
- Slow to converge

**OUTPUT STREAMS DEFINED**
- GOOD FOR DEALING WITH THE FUTURE

Long convergence times can be a problem (3-4 hours)
What actually happens when Aspen runs?

- What happens?
Each unit operation, flow stream, physical properties of each reactant, product and intermediate is run sequentially until convergence. Each possible ion species is solved for, including precipitation etc.

- How many equations?
A separate insight is available in the “equation oriented mode” where it can be seen that Aspen is solving 20,000 to 50,000 equations simultaneously.

- What is the result?
If the problem is “well-posed” i.e. the number of degrees of freedom is deliberately kept small, then the result is a rigorous imposition of a carefully designed mass and energy balance.
## Selected Results from Proactive Use of Aspen

**Full recycle, no lipid loss**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process operation</td>
<td>7,884</td>
<td>hour/year (90 %)</td>
</tr>
<tr>
<td>CO$_2$ removal</td>
<td>1,000,000</td>
<td>tonne/year CO$_2$</td>
</tr>
<tr>
<td>Insolation (Corpus Christi, TX)</td>
<td>4.2</td>
<td>kW h/m$^2$/day</td>
</tr>
<tr>
<td>Evaporation (Corpus Christi, TX)</td>
<td>1.27</td>
<td>m$^3$/hr/hec</td>
</tr>
<tr>
<td>Carbon conversion to biodiesel (9 M ethyl Esters)</td>
<td>95</td>
<td>wt %</td>
</tr>
<tr>
<td>Biodiesel produced (as 9 M ethyl Esters)</td>
<td>46.4</td>
<td>tonne/hr</td>
</tr>
<tr>
<td></td>
<td>2,630,450</td>
<td>barrel oil equivalent /yr</td>
</tr>
<tr>
<td>Total Area</td>
<td>20,033</td>
<td>hc</td>
</tr>
<tr>
<td>Reaction Operation 1 Area for algae generation</td>
<td>484</td>
<td>hc</td>
</tr>
<tr>
<td>Reaction Operation 2 Area for oil generation</td>
<td>19,549</td>
<td>hc</td>
</tr>
<tr>
<td>Oil productivity (based on total area)</td>
<td>5.6</td>
<td>g/m$^2$/day</td>
</tr>
<tr>
<td>Effective oil content</td>
<td>57%</td>
<td>wt%</td>
</tr>
<tr>
<td>Genetic stability requirements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Number of generations/year (binary fision)</td>
<td>43.6</td>
<td></td>
</tr>
</tbody>
</table>
Outputs from Aspen Model

The eighteen areas are:

1. Process Summary
2. Mass Balances
3. Energy Balance (1st Law)
4. Exergy (2nd Law)
5. Energy Analysis of Reactor 1
6. Energy Analysis of Reactor 2
7. Effluent/Bleed, Salinity, TDS
8. Water and Recycle
9. The Role of Evaporation
10. Control of Hazardous Precipitation of Inorganic Solids
11. Summary of Input and Output Streams
12. Photosynthetic Efficiency
13. Preliminary Check of Process Costs
14. Data Assembly for Flow Diagrams
15. Flow Diagrams:
   (i) Carbon
   (ii) Water
   (iii) Mass
   (iv) Enthalpy (1st Law of Thermodynamics)
   (v) Exergy (2nd Law of Thermodynamics)
   (vi) Exergy and Lost Work (2nd Law of Thermodynamics)
16. Establishing the Value Chain
17. The Value of Adding Extra Glycerol
18. Full Financial Analysis
Lesson Learned 4: This is an Energy Project

- funded by the Department of Energy

• Biofuels projects rely heavily on the science of energy aka thermodynamics.

• Aspen and other data bases have been vastly expanded with new versions but it is never enough.

• It is often necessary to calculate (because no-one has measured) $\Delta H_{\text{formation}}$ and $\Delta G_{\text{formation}}$ to establish heats of reaction.

$$\Delta H_{\text{reaction}} = \Delta H_{\text{formation. products}} - \Delta H_{\text{formation. reactants}}$$

• If running Aspen forwards (reactive) you mainly only need the thermodynamics of water.

• If running Aspen in reverse (proactive) then you need good data.
## Components and Their Properties

### Methyl Esters (FAME)

<table>
<thead>
<tr>
<th>Type</th>
<th>Common Name</th>
<th>Aspen Name</th>
<th>CAS No.</th>
<th>Formula</th>
<th>( \Delta H_f )</th>
<th>( S_f )</th>
<th>( \Delta G_f )</th>
<th>MW</th>
<th>Used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14:0</td>
<td>Methyl myristate</td>
<td>METHY-01</td>
<td>124-10-7</td>
<td>( C_{14} ) ( H_{28} ) ( O_2 )</td>
<td>-10,360.70</td>
<td>-759.40</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
</tr>
<tr>
<td>C16:0</td>
<td>Methyl palmitate</td>
<td>METHY-02</td>
<td>112-39-0</td>
<td>( C_{16} ) ( H_{34} ) ( O_2 )</td>
<td>-10,107.00</td>
<td>-1,441.80</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
</tr>
<tr>
<td>C16:1</td>
<td>Methyl palmitoleate</td>
<td>METHY-03</td>
<td>1120-25-8</td>
<td>( C_{16} ) ( H_{32} ) ( O_2 )</td>
<td>-14,208.90</td>
<td>-674.29</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
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<tr>
<td>C18:0</td>
<td>Methyl stearate</td>
<td>METHY-03</td>
<td>112-61-8</td>
<td>( C_{18} ) ( H_{36} ) ( O_2 )</td>
<td>-13,962.00</td>
<td>-945.60</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
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<tr>
<td>C18:1n9</td>
<td>Methyl oleate</td>
<td>METHY-04</td>
<td>2462-84-2</td>
<td>( C_{18} ) ( H_{34} ) ( O_2 )</td>
<td>-11,832.40</td>
<td>-789.27</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
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<tr>
<td>C18:2n6</td>
<td>Methyl linoleate</td>
<td>METHY-06</td>
<td>112-63-0</td>
<td>( C_{18} ) ( H_{32} ) ( O_2 )</td>
<td>-11,690.10</td>
<td>-604.88</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
</tr>
<tr>
<td>C20:4n6</td>
<td>Methyl arachidonate</td>
<td>METHY-07</td>
<td>2566-89-4</td>
<td>( C_{20} ) ( H_{44} ) ( O_2 )</td>
<td>-13,263.00</td>
<td>-1,003.00</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
</tr>
<tr>
<td>C20:5n3</td>
<td>Methyl eicosapentaen</td>
<td>METHY-08</td>
<td>2734-47-6</td>
<td>( C_{20} ) ( H_{44} ) ( O_2 )</td>
<td>-12,687.00</td>
<td>-1,003.00</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
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<tr>
<td>C22:1</td>
<td>Methyl erucinate</td>
<td>METHY-09</td>
<td>1120-34-9</td>
<td>( C_{22} ) ( H_{46} ) ( O_2 )</td>
<td>-14,451.50</td>
<td>-887.47</td>
<td>149</td>
<td>2000</td>
<td>NIST</td>
</tr>
</tbody>
</table>

### Triglycerides

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Aspen Name</th>
<th>CAS No.</th>
<th>Formula</th>
<th>( \Delta H_f )</th>
<th>( S_f )</th>
<th>( \Delta G_f )</th>
<th>MW</th>
<th>Used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimyristin</td>
<td>TRIMY-01</td>
<td>555-45-3</td>
<td>( C_{46} ) ( H_{87} ) ( O_6 )</td>
<td>-27,643.70</td>
<td>-2,355.00</td>
<td>370.82</td>
<td>2,725.82</td>
<td>NIST</td>
</tr>
<tr>
<td>Tripalmitin</td>
<td>TRIPA-01</td>
<td>555-44-2</td>
<td>( C_{52} ) ( H_{96} ) ( O_6 )</td>
<td>-31,605.90</td>
<td>-2,468.70</td>
<td>413.98</td>
<td>2,882.68</td>
<td>NIST</td>
</tr>
<tr>
<td>Tripalmitolein</td>
<td>TRIPA-02</td>
<td>118450-52-52</td>
<td>( C_{58} ) ( H_{110} ) ( O_6 )</td>
<td>-31,179.20</td>
<td>-2,030.00</td>
<td>370.82</td>
<td>2,725.82</td>
<td>NIST</td>
</tr>
<tr>
<td>Tristearin</td>
<td>TRIST-01</td>
<td>555-43-1</td>
<td>( C_{64} ) ( H_{128} ) ( O_6 )</td>
<td>-35,806.70</td>
<td>-2,801.14</td>
<td>457.14</td>
<td>2,882.68</td>
<td>NIST</td>
</tr>
<tr>
<td>Triolein</td>
<td>TRIOL-01</td>
<td>122-32-7</td>
<td>( C_{68} ) ( H_{136} ) ( O_6 )</td>
<td>-35,555.70</td>
<td>-1,880.10</td>
<td>450.93</td>
<td>2,331.03</td>
<td>NIST</td>
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<tr>
<td>Triarachidonate</td>
<td>TRIA-02</td>
<td>23314-57-0</td>
<td>( C_{84} ) ( H_{204} ) ( O_6 )</td>
<td>-39,467.70</td>
<td>-2,759.10</td>
<td>500.29</td>
<td>3,259.39</td>
<td>PPT</td>
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<td>Triecosapentanoate</td>
<td>TRAE-01</td>
<td>99660-94-3</td>
<td>( C_{86} ) ( H_{212} ) ( O_6 )</td>
<td>-38,761.44</td>
<td>-1,890.80</td>
<td>484.79</td>
<td>2,375.59</td>
<td>CS</td>
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<td>Trerucin</td>
<td>TRIEU-01</td>
<td>2752-99-0</td>
<td>( C_{92} ) ( H_{220} ) ( O_6 )</td>
<td>-42,802.30</td>
<td>-2,643.00</td>
<td>540.35</td>
<td>3,183.35</td>
<td>NIST</td>
</tr>
</tbody>
</table>

### Reliably Thermodynamic Data is hard to find.

Not all databases are created equal. Need to establish much from 1st principles.
Calculated Thermodynamic Properties of Algal Cells of Varying Oil Content

Nannochloropsis salina \((CH_{1.90}O_{0.40}N_{0.083}S_{0.0017}P_{0.002})\)

- \(\Delta G_{\text{formation}}\)
- \(\Delta H_{\text{formation}}\)
- \(\Delta H_{\text{combustion}}\)

Lipid content of algal cell, wt%
# Reactions with Corresponding Heats of Reaction

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reaction</th>
<th>ΔH kJ/mol</th>
<th>ΔG kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$46.29 \text{HCO}_3^- + 3.84 \text{NO}_3^- + 0.079 \text{SO}_4^{2-} + 0.093 \text{HPO}_4^{2-} + 46.02 \text{H}_2\text{O} \rightarrow 1 \text{Nanno} + 64.05 \text{O}_2 + 50.46 \text{OH}^-$</td>
<td>21,676</td>
<td>19,889</td>
</tr>
<tr>
<td>2</td>
<td>$15.4286 \text{Glycerol} + 3.8417 \text{NO}_3^- + 0.0926 \text{SO}_4^{2-} + 0.0926 \text{HPO}_4^{2-} \rightarrow 1 \text{Nanno} + 10.0502 \text{O}_2 + 15.6971 \text{H}_2\text{O} + 4.1842 \text{OH}^-$</td>
<td>-3,888</td>
<td>-6,682</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Deb80} \rightarrow \text{ALgDeb}$</td>
<td>4,778</td>
<td>4,344</td>
</tr>
<tr>
<td>4</td>
<td>$0.0216048 \text{NannoNew} + 0.0074 \text{NO}_3^- + 1.2708 \text{O}_2 \rightarrow +1 \text{CO}_2^- + 0.0017 \text{SO}_4^-- + 0.002 \text{HPO}_4^- + 0.949 \text{H}_2\text{O} + 0.0452 \text{N}_2$</td>
<td>-21,676</td>
<td>-21,264</td>
</tr>
<tr>
<td>5</td>
<td>$0.1296292 \text{NannoNew} + 0.0444 \text{NO}_3^- + 1.6248 \text{O}_2 + 0.306 \text{H}_2\text{O} \rightarrow +1 \text{SOLC}^- + 0.0102 \text{SO}_4^- + 0.012 \text{HPO}_4^- + 0.2712 \text{N}_2$</td>
<td>-1,148</td>
<td>-3,600</td>
</tr>
<tr>
<td>6</td>
<td>$0.65 \text{Nanno} + 22.3292 \text{HCO}_3^- + 0.0 \text{NO}_3^- + 20.4131 \text{H}_2\text{O} \rightarrow 1 \text{OC35} + 31.2653 \text{O}_2 + 22.3292 \text{OH}^- + 0.0 \text{SO}_4^- + 0.0 \text{HPO}_4^- + 22.3292 \text{OH}$</td>
<td>19,126</td>
<td>15,710</td>
</tr>
<tr>
<td>7</td>
<td>$0.3 \text{Nanno} + 44.6585 \text{HCO}_3^- + 40.8261 \text{H}_2\text{O} \rightarrow \text{OC70} + 62.5306 \text{O}_2 + 0.0 \text{NO}_3^- + 0.0 \text{SO}_4^{2-} + 0.0 \text{HPO}_4^- + 44.6585 \text{OH}^-$</td>
<td>24,993</td>
<td>19,042</td>
</tr>
<tr>
<td>8</td>
<td>$0.65 \text{Nanno} + 7.4431 \text{Gly} + +0.0 \text{SO}_4^{2-} + 0.0 \text{HPO}_4^- + 0.9942 \text{H}_2\text{O} \rightarrow 1 \text{OC35} + 9.3593 \text{H}_2\text{O} + 5.2145 \text{O}_2 + 0.0 \text{NO}_3^-$</td>
<td>1,973</td>
<td>1,209</td>
</tr>
<tr>
<td>9</td>
<td>$0.3 \text{Nanno} + 14.88616 \text{Gly}^- + 0.0 \text{SO}_4^{2-} + 0.0 \text{HPO}_4^- \rightarrow 1 \text{OC70} + 18.7185 \text{H}_2\text{O} + 10.4291 \text{O}_2 + 0.0 \text{NO}_3^-$</td>
<td>9,132</td>
<td>5,487</td>
</tr>
<tr>
<td>10</td>
<td>$0.95 \text{Nanno} + 0.0 \text{HPO}_4^- + 2.91615 \text{H}_2\text{O} + 3.18989 \text{HCO}_3^- \rightarrow 1 \text{OC5} + 4.4665 \text{O}_2 + 0.0 \text{SO}_4^- + 0.0 \text{NO}_3^- + 3.18989 \text{OH}$</td>
<td>2,276</td>
<td>1,740</td>
</tr>
<tr>
<td>11</td>
<td>$0.95 \text{Nanno} + 1.063297 \text{Gly} + 0.0 \text{SO}_4^{2-} + 0.0 \text{HPO}_4^- \rightarrow 1 \text{OC5} + 0.7449 \text{O}_2 + +1.3370 \text{H}_2\text{O}+0.0 \text{NO}_3^-</td>
<td>234</td>
<td>146</td>
</tr>
<tr>
<td>12</td>
<td>$0.0216048 \text{NannoNew} + 0.0074 \text{NO}_3^- + 1.2708 \text{O}_2 \rightarrow +1 \text{CO}_2^- + 0.0017 \text{SO}_4^- + 0.002 \text{HPO}_4^- + 0.949 \text{H}_2\text{O} + 0.0452 \text{N}_2$ (duplicate of Reaction 4)</td>
<td>-21,676</td>
<td>-21,264</td>
</tr>
<tr>
<td>13</td>
<td>$0.1296292 \text{NannoNew} + 0.0444 \text{NO}_3^- + 1.6248 \text{O}_2 + 0.306 \text{H}_2\text{O} \rightarrow +1 \text{SOLC}^- + 0.0102 \text{SO}_4^- + 0.012 \text{HPO}_4^- + 0.2712 \text{N}_2$ (duplicate of Reaction 5)</td>
<td>-1,148</td>
<td>-3,600</td>
</tr>
<tr>
<td>14</td>
<td>$\text{OC35} + 0.187970 \text{H}_2\text{O} \rightarrow 0.714286 \text{Debris} + 0.206767 \text{O}_2 + 0.390977 \text{TAG}$</td>
<td>-3,344</td>
<td>-3,083</td>
</tr>
<tr>
<td>15</td>
<td>$1.4 \text{OC70} + 0.4 \text{H}_2\text{O} \rightarrow 0.4 \text{Debris} + 0.3 \text{O}_2 + \text{TAG}$</td>
<td>-1,899</td>
<td>-1,768</td>
</tr>
<tr>
<td>16</td>
<td>$\text{OC5} + 0.031328 \text{H}_2\text{O} \rightarrow 1.285714 \text{Debris} + 0.31328 \text{O}_2 + 0.065163 \text{TAG}$</td>
<td>-6,131</td>
<td>-4,963</td>
</tr>
</tbody>
</table>
Lesson Learned 5: Handling Complex Stoichiometry

Balancing the stoichiometry of these equations is a fast route to insanity.
Example:
a OC\textsubscript{70} + b \text{Debris} + c O\textsubscript{2} + d H\textsubscript{2}O + e SO\textsubscript{4}\textsuperscript{2-} + f HPO\textsubscript{4}\textsuperscript{2-} \rightarrow TAG9

**INPUT MATRIX** [A]

<table>
<thead>
<tr>
<th></th>
<th>OC\textsubscript{70}</th>
<th>Debris</th>
<th>O\textsubscript{2}</th>
<th>H\textsubscript{2}O</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>HPO\textsubscript{4}\textsuperscript{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>58.5501</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>107.955</td>
<td>1.9</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>10.6368</td>
<td>0.4</td>
<td>2</td>
<td>1</td>
<td>4</td>
<td>4</td>
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<tr>
<td>N</td>
<td>1.1525</td>
<td>0.083</td>
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<td>0</td>
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<tr>
<td>S</td>
<td>0.02368</td>
<td>0.0017</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>P</td>
<td>0.02780</td>
<td>0.002</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

**RESULT VECTOR** [B]

<table>
<thead>
<tr>
<th></th>
<th>TAG9</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC\textsubscript{70}</td>
<td>63.83</td>
</tr>
<tr>
<td>Debris</td>
<td>116.21</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>7.263</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>0</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>0</td>
</tr>
<tr>
<td>HPO\textsubscript{4}\textsuperscript{2-}</td>
<td>0</td>
</tr>
</tbody>
</table>

**INVERSE MATRIX** [A\textsuperscript{-1}]

\[
\begin{bmatrix}
0.022389 & 1.51E-21 & 0 & -0.269 & 0 & 3.5E-17 \\
-0.31089 & 1.01E-17 & 0 & 15.793 & 0 & -2.1E-15 \\
0.399691 & -0.25 & 0.5 & -1.420 & -2 & -1.75 \\
-0.91317 & 0.5 & 0 & -0.432 & 0 & -0.50 \\
-1.7E-06 & -3.8E-19 & 0 & 0.020 & 1 & 4.3E-19 \\
-6.5E-07 & -1.6E-19 & 0 & -0.024 & 0 & 1
\end{bmatrix}
\]

**SOLUTION VECTOR** [X]

<table>
<thead>
<tr>
<th></th>
<th>OC\textsubscript{70}</th>
<th>Debris</th>
<th>O\textsubscript{2}</th>
<th>H\textsubscript{2}O</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>HPO\textsubscript{4}\textsuperscript{2-}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.429097</td>
<td>-19.84379</td>
<td>0.091596</td>
<td>-0.183107</td>
<td>-0.00011</td>
<td>-4.13E-05</td>
</tr>
<tr>
<td>b</td>
<td>-0.91317</td>
<td>0.5</td>
<td>0</td>
<td>-0.432</td>
<td>0</td>
<td>-0.50</td>
</tr>
<tr>
<td>c</td>
<td>-1.7E-06</td>
<td>-3.8E-19</td>
<td>0</td>
<td>-0.020</td>
<td>1</td>
<td>4.3E-19</td>
</tr>
<tr>
<td>d</td>
<td>-1.6E-19</td>
<td>0</td>
<td>-0.024</td>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\([A][X]=[B]\) or \([X]=[A\textsuperscript{-1}][B]\)

A positive coefficient in the solution vector denotes a reactant, while a negative coefficient denotes a product.

Thus the balanced equation for this example is :-

\[
1.429097 \text{OC70} + 0.091596 \text{O}_2 \rightarrow \text{TAG9} + 19.84379 \text{Debris} + 0.183107 \text{H}_2\text{O} + 0.00011 \text{SO}_4^{2-} + 4.13E-05 \text{HPO}_4^{2-}
\]
Lesson Learned 6: 2nd Law and Lost Work

As this is a Second Law of Thermodynamics Analysis it needs $\Delta G$ and hence $\Delta S$. Entropy measurements are in total disarray... if they even exist.
Lesson Learned 7: Pipes & Pumps

Get the pipes and pumps in early.

This is not normal practice, but with algae processes, they consume so much energy and capex that the sooner they are identified the better.
Chapter 1.4  Setting up Aspen Pipes & Pumps in Aspen Process Flow Diagram
Lesson Learned 8: Liquifaction

As we move away from the “simple” systems of biodiesel and its components, we enter another difficult area.

Namely the hundreds of components that form, at different temperatures and pressures, as the biomass is liquified.

Multiple reaction schemes are being investigated.

How to deal with that in a TEA?
Lesson Learned 8: RGibbs

- RGibbs usually overlooked.

- All the others require knowledge of complex reaction stoichiometry and rate constants, none of which we usually have.

- RGibbs treats all components, reactants and products, as potential products and calculates the product mix that minimizes the Gibbs Free Energy. This is what nature does anyway! But we do need the ΔH and ΔG as a function of temperature and pressure, usually calculable.

“Einstein: God integrates empirically”. This must be the next best thing.
Lesson Learned 9: Number of Organism Generations

\[ \frac{N(t)}{N(0)} = 2^n \quad \text{(binary fission)} \]

\[ \approx 40+ \text{ generations} \]

An unexpected output from Aspen.

Sets the target for the stability of genetically modified organisms that may subsequently be used.
Lesson Learned 10: Costing Accuracy comes at a (very) high cost.

<table>
<thead>
<tr>
<th>Study/Design</th>
<th>Probable Range of Accuracy</th>
<th>Cost as % of Project Expenditure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Preliminary Costing</td>
<td>30% to 50%</td>
<td>0.05% to 0.1%</td>
</tr>
<tr>
<td>2 Design Study</td>
<td>20% to 30%</td>
<td>0.1% to 0.2%</td>
</tr>
<tr>
<td>3 Preliminary Construction Estimate</td>
<td>10% to 25%</td>
<td>0.4% to 0.8%</td>
</tr>
<tr>
<td>4 Definitive Estimate</td>
<td>5% to 15%</td>
<td>1% to 3%</td>
</tr>
<tr>
<td>5 Detailed Estimate</td>
<td>2% to 5%</td>
<td>5% to 10%</td>
</tr>
</tbody>
</table>

Lesson 10a.
Beware of any TEA that does not come with error bars.
Approach to Cost Financial Modeling

Costing Model $\rightarrow$ Financial Model

Revenues & Costs $\rightarrow$ Operating Margins

Cash Flow Analysis. How many plants, what size, when on line

Cost of capital, depreciation, taxation, tax shields, investment credits etc.
$\rightarrow$ Range of cash flows

Financial Metrics (M)IRR, NPV etc.

Taxation has the potential to add significant cost OR tax shields may allow major cost reductions
Lesson Learned 11: All TEA “unit costs” are not the same.

**ESTIMATED OPERATING MARGINS ($)**

**REVENUES**
- Selling Price per barrel ($120)
- no. of new plants
- total number of plants
- % of CO2 market
- oil production, barrels/ year
- % US consumption
- Revenue

**EXPENSES**
- VARIABLE COSTS (VC)
  - Raw materials cost/yr
  - Utility costs/yr (@ 10% raw material costs)
  - Labor costs (@ 10% raw material costs)
  - Workman’s Comp & Unemployment Tax (@10% of Labor Costs)
- FIXED COSTS (FC)
  - Supervisory/ mgmt costs/yr
  - Cost of sales (6% of actual sales)
  - Insurance (5% of sales)
  - Plant overhead (5% of sales)
  - Total costs (VC+FC)

**OPERATING MARGIN**
(revenue - costs)

**CASH FLOW ANALYSIS**

- Estimated cost of capital, 15%
- PROJECT DEVELOPMENT PHASES
  - Development Phase
  - Plant Construction & Operating phase
    - No. of new plants
    - Capital cost of plant
    - Cost of capital
    - Start up costs, 5% of capital
    - Maintenance, 5% of capital
    - Working capital, 10% of capital
    - Salvage value, 5% of capital cost
- Plant Depreciation (straight line 25 years)
- Total Operating costs
- Net operating cash flow
- TAX SHIELDS; 35% tax
- Depreciation (25 year straight line)
- Investment Tax Credit (10%)
- Taxable income
- TAX @ 35%
- Total tax shield

**AFTER TAX CASH FLOW**

**FINANCIAL METRICS**

- (M) IRR %
- Finance Rate 15.00%
- Reinvest Rate 5.00%
- NPV $xxE+y
  @ 25.00% discount rate

**FINANCIAL/INVESTMENT MODEL FLOWS**

- **P:E** 10
- Market cap. Million $
- Economy of scale over 25 years
- Total oil produced 1.3E+09 barrels
- Total costs $1.2E+x
- Effective cost $xx/bbl
  $yy/gallon
  ±100%

ABO Algal Biomass Summit, San Diego, October 2014
Lesson Learned 12: Missing information can be found by using other simulation tools

The Case for Comsol: Depth, Light Scattering & Non-steady State Models

GROWTH RATE and its Distribution within the reactor vs Time
Conclusions

- These are very personal observations on trying to do Techno-Economic Analyses for algal processes & don’t suit everybody.

- Each lesson we learned contributes to an integrated systems approach to algal biofuel production.

- When each lesson is fully implemented into a process simulation such as AspenPlus, the result is more than the sum of the parts.
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2. Contract DE-EE0006316 awarded to the research project, Realization of Algae Potential.