Growing and Converting Aquatic Biomass for Fuel Precursors
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Sunrise Ridge Algae

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To secure a high value position in the energy value chain, we sought to generate and transform a new feedstock.
Who we have been.

- Private Texas corporation engaged in R&D and commercialization of algae biomass technology
  - reduction of water & greenhouse gas pollutants
  - production of renewable fuel, feedstocks and animal feeds.
- Owned and operated a pilot production facility in Katy, Texas.
- Academic Collaborations
  - UTEX (Prof. Jerry Brand, UT)
  - CAE (Prof. Kerry Kinney, UT)
  - SRP (Prof. Frank Siebert, UT)
  - Prof. Mike Harold UH)

Funded by

- Private investment
- Current grant from Texas Emerging Technology Fund (extension pending)
- Federal agencies
- Sales of services
Once-upon-a-time, we liked algae-derived fuels.

Postives:
- Potentially scalable
- Don’t compete with food
- Do not require arable land
- Water sparing

Negatives:
- Dilute (~1 g/L)
- Require stirring & gas delivery
- Hard to harvest (1-3 µm)
- Nutrient recycling
Our first pilot plant was located at Hornsby Bend Wastewater Treatment Plant, Austin, TX...
… where we devised production-scale helioreactors and protocols for harvesting algae.

- Each contains, 25,000 L and has 90 m² of solar area
- Each produces about 1-3 kg algae per week
- Low productivity (5 g/m²/day; 0.1 g/L) ascribed to intermittent supply of CO₂.
- Technology applicable to other sites, including CAFOs and industrial facilities.
We got as far as piloting both farm and conversion operations

<table>
<thead>
<tr>
<th>2009-2010</th>
<th>2010</th>
<th>2011</th>
<th>2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab</td>
<td>Pilot Project</td>
<td>Semi-Works Project</td>
<td>1st Commercial Site</td>
</tr>
<tr>
<td>0.000001 acre</td>
<td>~0.1 acre</td>
<td>~10 acre</td>
<td>~600 acre</td>
</tr>
<tr>
<td>500 K$</td>
<td>5-10M$</td>
<td>50 - 100 M$</td>
<td>200-500 M$?</td>
</tr>
<tr>
<td>1 L/day</td>
<td>1 bbl/day</td>
<td>600 bbl/day</td>
<td>6000 bbl/day</td>
</tr>
</tbody>
</table>
But, we did not find a viable path for this, the 4th, 30-year cycle of biofuels since 1920.

- The goal is still renewable fuels at economic par with petrofuels, without additional externalities.
- We doubt that genetic engineering will have the needed impact.
- We expect that integration with the existing industrial ecology will be critical to the solution.
- We expect that the most effective crop will be aquatic, not terrestrial.
- We believe that conversion will involve thermochemical upgrading, not extraction and transformation of lipids.
- However, we believe that chemical engineering is not yet on the critical path.
## The “Standard Model” is not a viable route to introduction of algae-derived fuels

### Components of the Standard Model

- Select or engineer algae to produce high lipids
- Grow and harvest the algae
- Sell non-lipid fraction into animal feed markets.
- Extract the lipids and make biodiesel.

### Issues

- Monocultures of GM algae are not robust.
- Costs are high: sterilization, delivery of CO₂, nutrients and controls, Water
- Feed market is not commensurate with full scale fuel production.
- Triglyceride intermediate is a bottleneck; biodiesel is not a fungible fuel

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It is unclear that genetic modifications that are being considered will assist materially.

- The immense scale of fuel-growing precludes sterilization and exclusion of competing species.

  Recirculation zones near the hairpin turns in a racetrack are likely harbors for dysbionts.

- Modifications that enhance production of exported energy molecules divert metabolic energy and therefore:
  - Diminish the fitness of the organism
  - Creates a locus for natural selection
  - May attract dysbionts.
Integrated Production is needed to control costs and provide maximum environmental benefits.

Our Focus

- Species + Nutrients
- Waste Heat
- Vented CO₂
- Aquatic Biomass Farm
- Separations & Processing
- Waste Water
- Waste Treatment
- Product Logistics

Services from industrial partners

Process integration is key
The feed market is not commensurate with the fuel market.

<table>
<thead>
<tr>
<th>Material</th>
<th>Consumption rate in the US/T d(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude petroleum</td>
<td>(3.2 \times 10^6)</td>
</tr>
<tr>
<td>Animal Protein forage (Pimentel)</td>
<td>(8.8 \times 10^5)</td>
</tr>
<tr>
<td>Biomass-derived feed available if biomass (at 10% lipid yield) were used to provide 10% oil in US</td>
<td>(2.9 \times 10^5)</td>
</tr>
</tbody>
</table>


So the market price for feed will likely become elastic when biomass-to-fuel supplies even a small fraction of the US market for fuel.
We investigated in detail an integration with a cement plant to produce fuel and GHG credits.

- Cement manufacturing creates about 0.9 T CO₂ per ton of cement along with copious quantities of waste heat.
- Cement sells for ~$90/T; CO₂ credits on the European market have ranged between €10-€35/T so inside-the-fence CO₂ offsets should be cost effective.

One form of integration:

New Facility Algae Operations

Existing Cement Plant

CO₂

Waste Heat

Char - Coal Substitute

Renewable Power

Bioleum

Crude Oil Substitute

Sell to Utility

Sell to Refinery

Sell to

Refinery
A cement plant has inputs and output streams that complement those of the production of renewable fuels.

Fun Facts about cement

<table>
<thead>
<tr>
<th>Stream</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>&gt;1 MT/y/plant</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.9 T/T</td>
</tr>
<tr>
<td>Fuel</td>
<td>5.5 GJ/T</td>
</tr>
</tbody>
</table>
Putting it all together

Our process took heat, CO$_2$ and water from the host site and returned water and fuel, minimizing emissions.
The algae side of the process

The process included three groups of algae operations: growth, harvesting and processing.

Cultivation: Gas dissolution, Cooling, Cultivation

Dewatering: Dissolved gas floatation, Belt press, Dryer

Processing: Thermolysis, Separations, Waste handling

inputs: CO₂, Nutrients, Water

outputs: Py-gas, Water, Bioleum, Char

Recycled Water
The algae-to-fuel process couples two recycle loops: water and char.

- Helioreactors designed for a residence time of 1 day
- Harvest rate = 0.75 (which leaves enough seed algae to restore the population at a doubling rate of twice per day)
- Char recycle of 0.1 (sufficient to deoxygenate and preheat the sweep gas)
- Blowdown estimated to be 10% of water recycle (to remove accumulated salts, etc).
We used Unisym to size the equipment and to close the mass and energy balances around the process.

### Power inputs for the 0.5 T/day design

<table>
<thead>
<tr>
<th>Operation</th>
<th>Electricity/kW</th>
<th>Thermal/kW</th>
<th>Estimation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water movement</td>
<td>1.9</td>
<td></td>
<td>Pressure head</td>
</tr>
<tr>
<td>Gas delivery</td>
<td>1.1</td>
<td></td>
<td>Pressure head</td>
</tr>
<tr>
<td>Harvesting</td>
<td>2</td>
<td></td>
<td>Vendor estimate</td>
</tr>
<tr>
<td>Filtration</td>
<td>3.1</td>
<td></td>
<td>Vendor estimate</td>
</tr>
<tr>
<td>Drying</td>
<td>1</td>
<td>13.7</td>
<td>Vendor + $\Delta H_{vap}$</td>
</tr>
<tr>
<td>Conversion</td>
<td>1</td>
<td>3</td>
<td>Vendor estimate + $C_p\cdot\Delta T$</td>
</tr>
<tr>
<td>Total</td>
<td>10.1</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>Fractional energy input (a)</td>
<td>10.6%</td>
<td>17.5%</td>
<td></td>
</tr>
</tbody>
</table>

### Aqueous flows for the 0.5 T/day design

<table>
<thead>
<tr>
<th>Input streams</th>
<th>Mass flows/kg h(^{-1})</th>
<th>Output streams</th>
<th>Mass flows/kg h(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas</td>
<td>78</td>
<td>Helioreactor(^{TM}) vent</td>
<td>5</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>10</td>
<td>DGF vent</td>
<td>0</td>
</tr>
<tr>
<td>Makeup water</td>
<td>1,092</td>
<td>Dryer vent</td>
<td>18</td>
</tr>
<tr>
<td>Beltpress wash</td>
<td>200</td>
<td>Pond vent</td>
<td>1,045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Blowdown</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pywater+Pygas+flare</td>
<td>7</td>
</tr>
<tr>
<td>Total</td>
<td>1,380</td>
<td></td>
<td>1,380</td>
</tr>
</tbody>
</table>
All major units for the pilot plant was available commercially, had been tested at scale, or were project foci

<table>
<thead>
<tr>
<th>Unit operation</th>
<th>Equipment</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas treatment</td>
<td>Gas washer, pumps compressors</td>
<td>Commercial</td>
</tr>
<tr>
<td>Water treatment</td>
<td>Mixers, nitrifiers</td>
<td>Commercial</td>
</tr>
<tr>
<td>Algae cultivation</td>
<td>SRA helioreactors</td>
<td>Tested at pilot scale</td>
</tr>
<tr>
<td>Algae harvesting</td>
<td>Dissolved Gas Flotation; Belt press</td>
<td>Commercial</td>
</tr>
<tr>
<td>Algae drying</td>
<td>Rotary dryer</td>
<td>Commercial</td>
</tr>
<tr>
<td>Thermolysis</td>
<td>Kiln, Condenser</td>
<td>Commercial, to be tested</td>
</tr>
<tr>
<td>Waste disposal</td>
<td>Flare</td>
<td>Commercial</td>
</tr>
<tr>
<td>Power generation</td>
<td>Turbine gen set</td>
<td>Commercial</td>
</tr>
</tbody>
</table>
At 0.5 T/day the algae cultivation, harvesting and processing could be sited on ~7 acres near the cement plant.
**Benefits of CO₂ via algaculture**

Estimated lifecycle greenhouse gas emission reductions

<table>
<thead>
<tr>
<th>Electricity source</th>
<th>Grid Power Co-Product Methods for bio-coal and Pygas</th>
<th>Bioleum Gen Set Allocation</th>
<th>Hybrid Substitution</th>
<th>U.S. Average Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Uptake</td>
<td>-73.0</td>
<td>-73.0</td>
<td>-73.0</td>
<td>Crude Extraction</td>
</tr>
<tr>
<td>Electric power, combustion</td>
<td>13.1</td>
<td>0.075</td>
<td>0.2</td>
<td>Crude Transport</td>
</tr>
<tr>
<td>Oil Transport</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Refinery Co-processing</td>
<td>13.6</td>
<td>13.6</td>
<td>13.6</td>
<td>Crude Refining</td>
</tr>
<tr>
<td>Fuel T&amp;D</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>Diesel T&amp;D</td>
</tr>
<tr>
<td>Fuel Combustion</td>
<td>73.8</td>
<td>73.8</td>
<td>73.8</td>
<td>Fuel Combustion</td>
</tr>
<tr>
<td>Thermolysis Fuel Credit</td>
<td></td>
<td></td>
<td>-494</td>
<td></td>
</tr>
<tr>
<td><strong>Total (g CO₂e/MJ)</strong></td>
<td>28.5</td>
<td>15.5</td>
<td><strong>-479</strong></td>
<td><strong>Total Fuel Cycle</strong></td>
</tr>
<tr>
<td><strong>% Reduction from Petro-Diesel</strong></td>
<td><strong>69.3%</strong></td>
<td><strong>83.4%</strong></td>
<td><strong>616%</strong></td>
<td>% Reduction from Petro-Diesel</td>
</tr>
</tbody>
</table>

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...as well as favorable economics compared to other approaches to CO₂ abatement.
At full scale to make a significant amount of crude oil we would have circulated a lot of water and occupied a lot of land:

- Design assumption: capture >70% of the emitted CO$_2$:

\[
\frac{1 \times 10^6 T_{\text{Cement}}}{365 \text{day/} y} \times \frac{0.9 T_{\text{CO}_2}}{T_{\text{cement}}} \times 0.7 \frac{T_{\text{algae}}}{1.8 T_{\text{CO}_2}}
\]

\[= 960 T_{\text{algae}} / \text{day}\]

\[\times 0.25 T_{\text{bioleum}} / T_{\text{algae}} \times 6.1 \text{bbl/} T = 1500 \text{bbl/} \text{day}\]

\[\times \frac{1 \text{day} - m^2}{30 \times 10^{-6} T_{\text{algae}}} \times \frac{1 \text{hectare}}{10^4 m^2} = 3200 \text{ha} = 7700 \text{acre}\]

\[\times \frac{1 L_{\text{water}}}{0.1 \times 10^{-6} T_{\text{algae}}} = 9.6 \times 10^9 L_{\text{water}} / \text{day} = 110 \times 10^6 \text{gal}_{\text{water}} / \text{h}\]
Testing component processes at pilot scale and verifying algaculture using real flue gas did not guarantee success.

**Biological/Ecological phenomena to be tested at scale**

- Principal species of algae, their growth rates and composition
- Sequestration of undesired (RCRA metals)
- Effects of predators, dysbionts, symbionts
- Availability of bioflocculants (important for harvesting)
- Rates of fouling
- Recycle-dependent phenomena
- Effects of upsets at the cement plant
Thermochemical upgrading can convert even low lipid biomass into bioleum, a high energy density crude.

### Characteristics of Bioleum

<table>
<thead>
<tr>
<th>Material</th>
<th>HHV/MJ kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude petroleum</td>
<td>45-48</td>
</tr>
<tr>
<td>Jet fuel (minimum)</td>
<td>43</td>
</tr>
<tr>
<td>Refined biodiesel</td>
<td>38</td>
</tr>
<tr>
<td>Algae-derived bioleum</td>
<td>36</td>
</tr>
<tr>
<td>Cellulose-derived py-oil</td>
<td>13-18</td>
</tr>
</tbody>
</table>

- Produced in a flow reactor at moderate temperatures (<450°C) and atmospheric pressure
- Yields of ~25wt% from algae that contain <5wt% lipids.
- Captures ~50% of the heating value of the input algae
- Product is high in N but low in P and S
- Processable in a conventional refinery along with VGO (adding “only” 6000 scf H₂/bbl)
High protein, low cellulosic algal biomass thermolyzes very differently from cellulosic biomass.

- We obtain a complex crude oil that exhibits a high heating value, very low sulfur but still high N- and O-contents
  - We speculate that the reaction proceeds first by the Maillard reaction and then via Amadori rearrangement products that eliminate oxygen as water.

- Use of a zeolite catalyst and CO\textsubscript{2} sweep gas affords high conversion at much lower temperatures (<300°C) and lower pressure (~1 atm) than are typical of pyrolysis of cellulosics or hydrothermal processing of algae.
  - We speculate that our process benefits from the effective use of the highly dispersed, naturally incorporated catalysts.

- Bioleum requires “only” ~3000 scf/bbl of H\textsubscript{2} for upgrading
Reaction (catalysis) engineering and reactor engineering are needed to engender fieldable upgrading operations:

- Efficient concentration of energy products
- Avoidance of waste streams (e.g., dirty water)
- Recovery of nutrients (N, P, trace metals) in a form that can be recycled
- Diversion of undesired biomass component (Hg, As, Pb, etc)
Thermolysis permits the use of other types of aquatic plant, e.g., the lemnaceae.

- Lemnaceae (duckweed) include many native species
- They grow rapidly, doubling in about 1.5 day (algae can double twice per day)
- Like algae, they denitrify the water.
- They are macroscopic and thus easy to harvest.
- Areal growth rates >50 dryT/hectare/year (=0.1 bbl/ha/day)

A crop for the whole family
Aquatic species help address the problem of limited water availability.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Areal yield bbl h^{-1}y^{-1}</th>
<th>“Blue” Water intensity c L L^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetable oil ex soybeans</td>
<td>2^a</td>
<td>6155</td>
</tr>
<tr>
<td>Pyrolysis oil ex wood</td>
<td>2^b</td>
<td>2600</td>
</tr>
<tr>
<td>Algae</td>
<td>300</td>
<td>200 est</td>
</tr>
<tr>
<td>Bioleum ex lelma (est.)</td>
<td>60</td>
<td>–400 est</td>
</tr>
</tbody>
</table>

b) Estimated from irrigation requirements and areal forestry yields in R. J. Zomer, et al., http://www.iwmi.cgiar.org/Publications/IWMI_Research_Reports/PDF/PUB122/RR122.pdf, and published yields of pyrolysis oil yields of “green” diesel

<table>
<thead>
<tr>
<th>Fluid</th>
<th>US consumption/L day^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum (20 million bbl/day)</td>
<td>10</td>
</tr>
<tr>
<td>Water (410 Bgal/day)</td>
<td>5000</td>
</tr>
</tbody>
</table>

So, replacement of ~10% of the US fuel supply with fuels derived from soybeans or wood could significantly increase water usage.
The design exercise taught us three important lessons about farming, biomass conversion and the value chain.

- Combinations of feedstocks may address the issue of limited water availability and can confer robustness
- Thermochemical processing of proteinaceous biomass is different from pyrolysis of cellulosic biomass
- Thermochemical upgrading broadens the available feedstocks and harvesting technologies
- Thermochemical upgrading affords opportunities for integration and CO₂ avoidance, particularly compared to the Standard Model
- Processing bioleum in a conventional refinery could be a quick and economical way of producing truly fungible fuels, if you have scale.
- Novel preprocessing of the bioleum in the field (adjacent to the growing facility) will be critical to the economics and efficiency.
We are grateful to our funders and to our partners for their thorough and timely assistance.

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- **A cement company in central Texas**