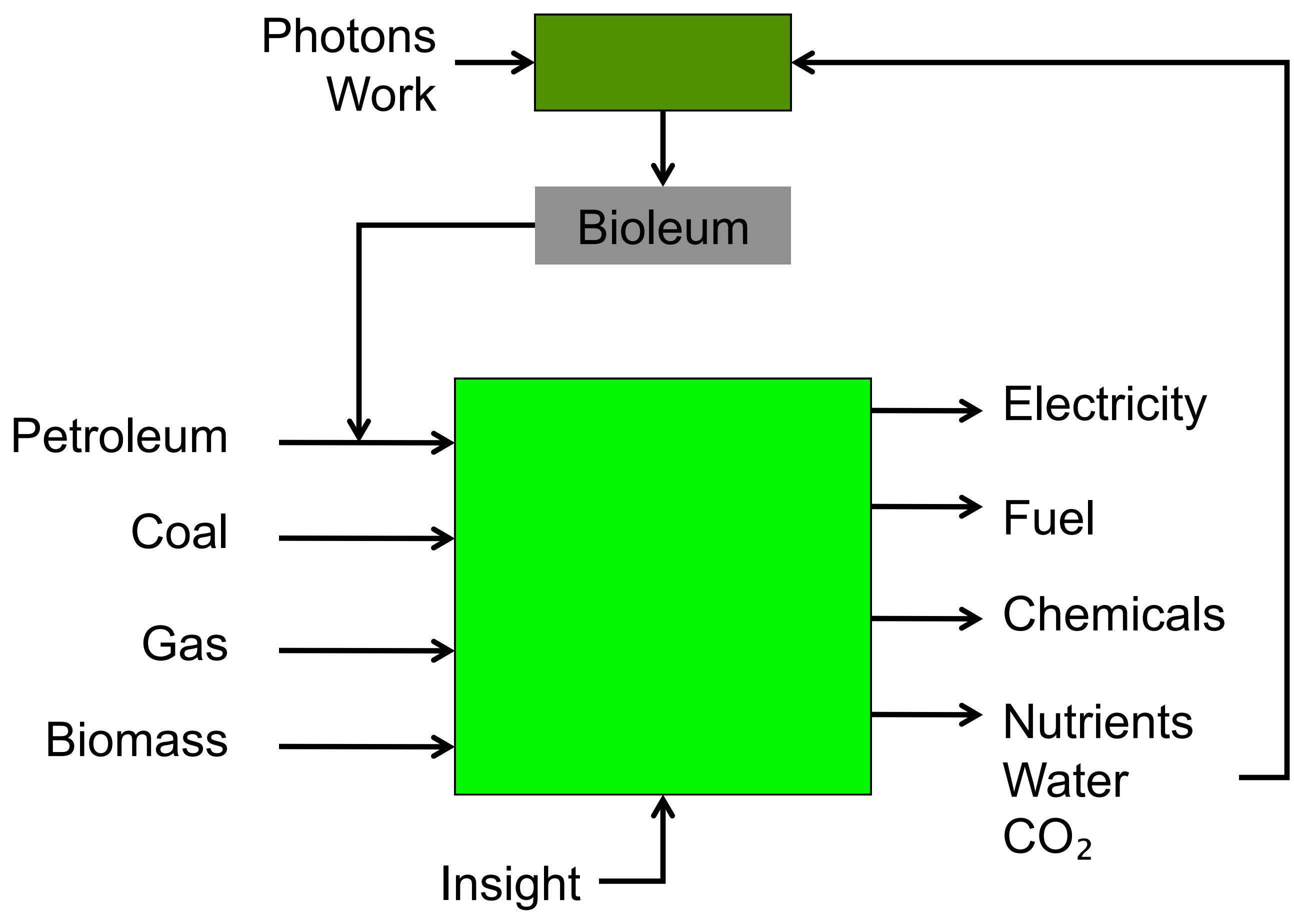
Growing and Converting Aquatic Biomass for Fuel Precursors

Robert S. Weber

Sunrise Ridge Algae

NIChE Workshop
21-22 September 2011

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.

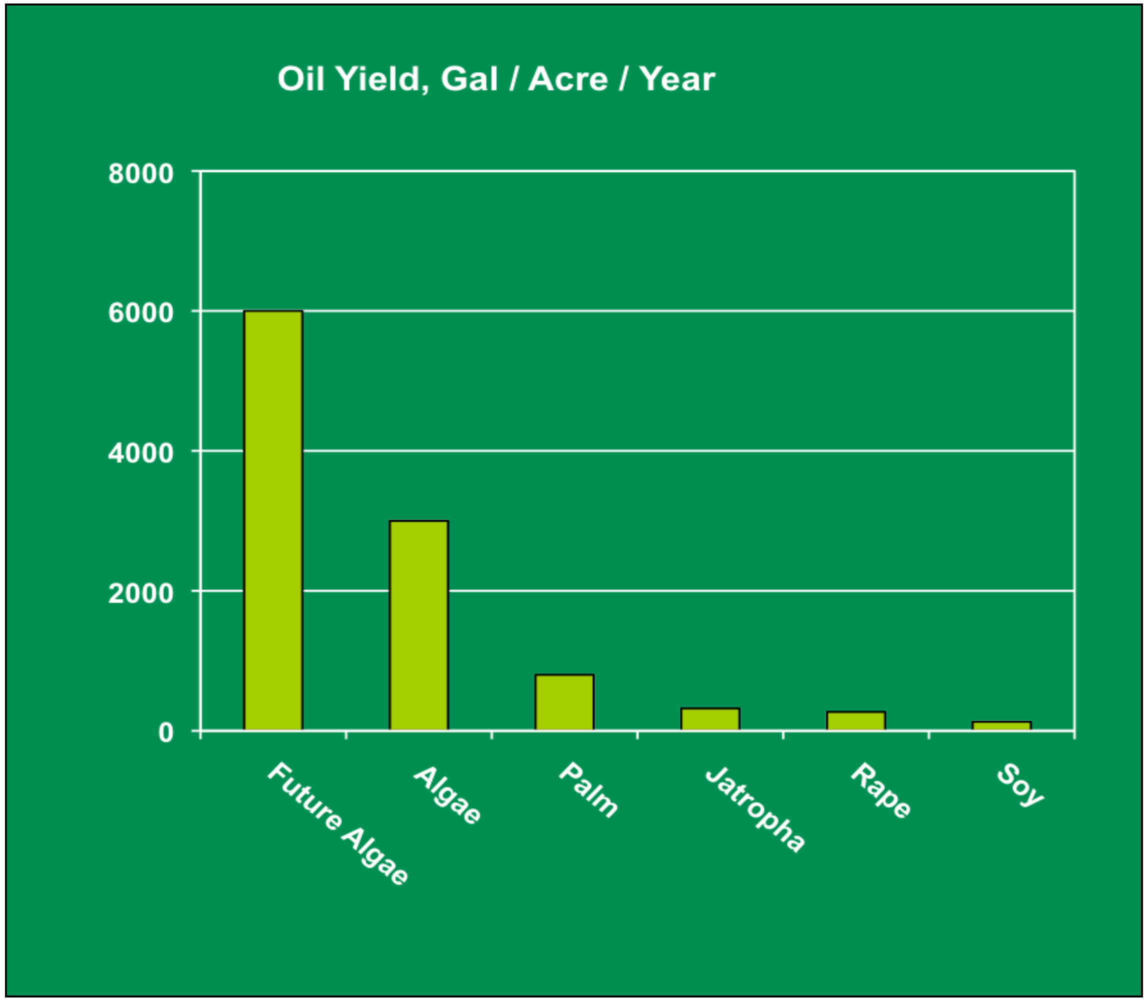
Sunrise Ridge

Postives:

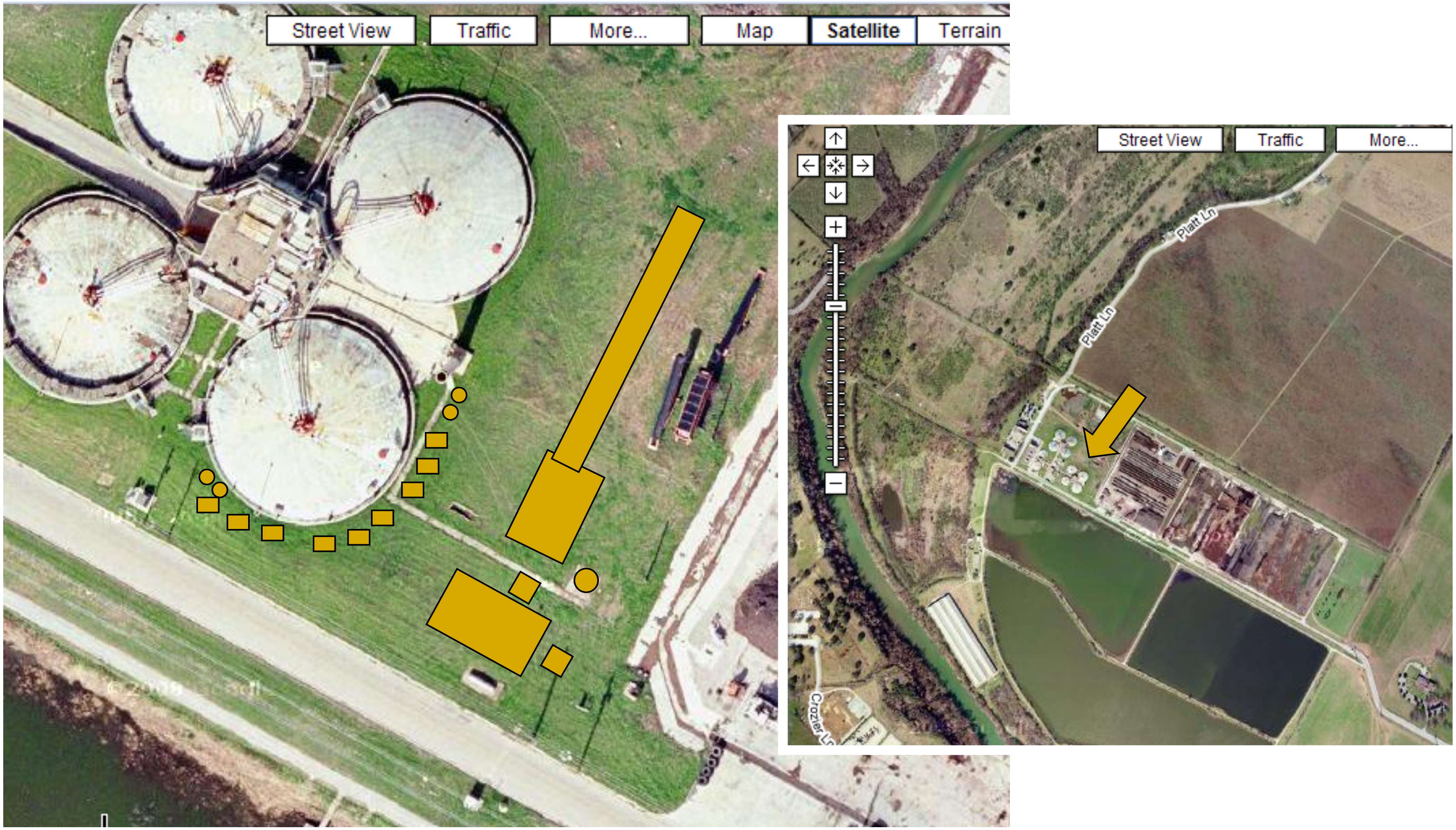
- **Potentially scalable**
- **Don't compete with food**
- **Do not require arable land**
- **Water sparing**

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…

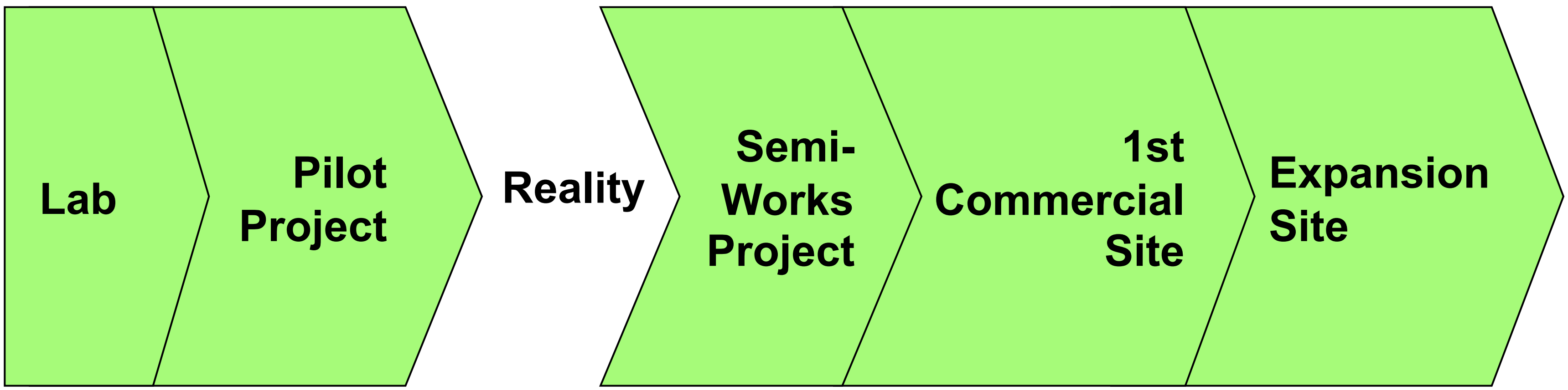


… where we devised production-scale helioreactors and protocols for harvesting algae.

- Each contains, 25,000 L and has 90 m^2 of solar area
- Each produces about 1-3 kg algae per week
- Low productivity (5 $g/m^2/day$; 0.1 g/L) ascribed to intermittent supply of CO_2.
- Technology applicable to other sites, including CAFOs and industrial facilities.

25,000 L Boomer™ production scale algae greenhouse (left)

We got as far as piloting both farm and conversion operations



	2009-2010	2010	2011	2013
0.00001 acre	~0.1 acre	~10 acre	~600 acre	~6000 acre
	500 K$	5-10M$	50 - 100 M$	200-500 M$?
	1 L/day	1 bbl/day	600 bbl/day	6000 bbl/day

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.

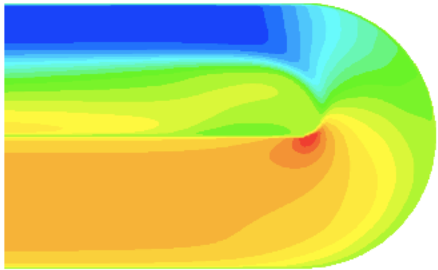
The "Standard Model" is not a viable route to introduction of algae-derived fuels

Sunrise Ridge

Components of the Standard Model	Issues
Select or engineer algae to produce high lipids	Monocultures of GM algae are not robust.
Grow and harvest the algae	Costs are high: sterilization, delivery of CO_2, nutrients and controls, Water
Sell non-lipid fraction into animal feed markets.	Feed market is not commensurate with full scale fuel production.
Extract the lipids and make biodiesel.	Triglyceride intermediate is a bottleneck; biodiesel is not a fungible fuel

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

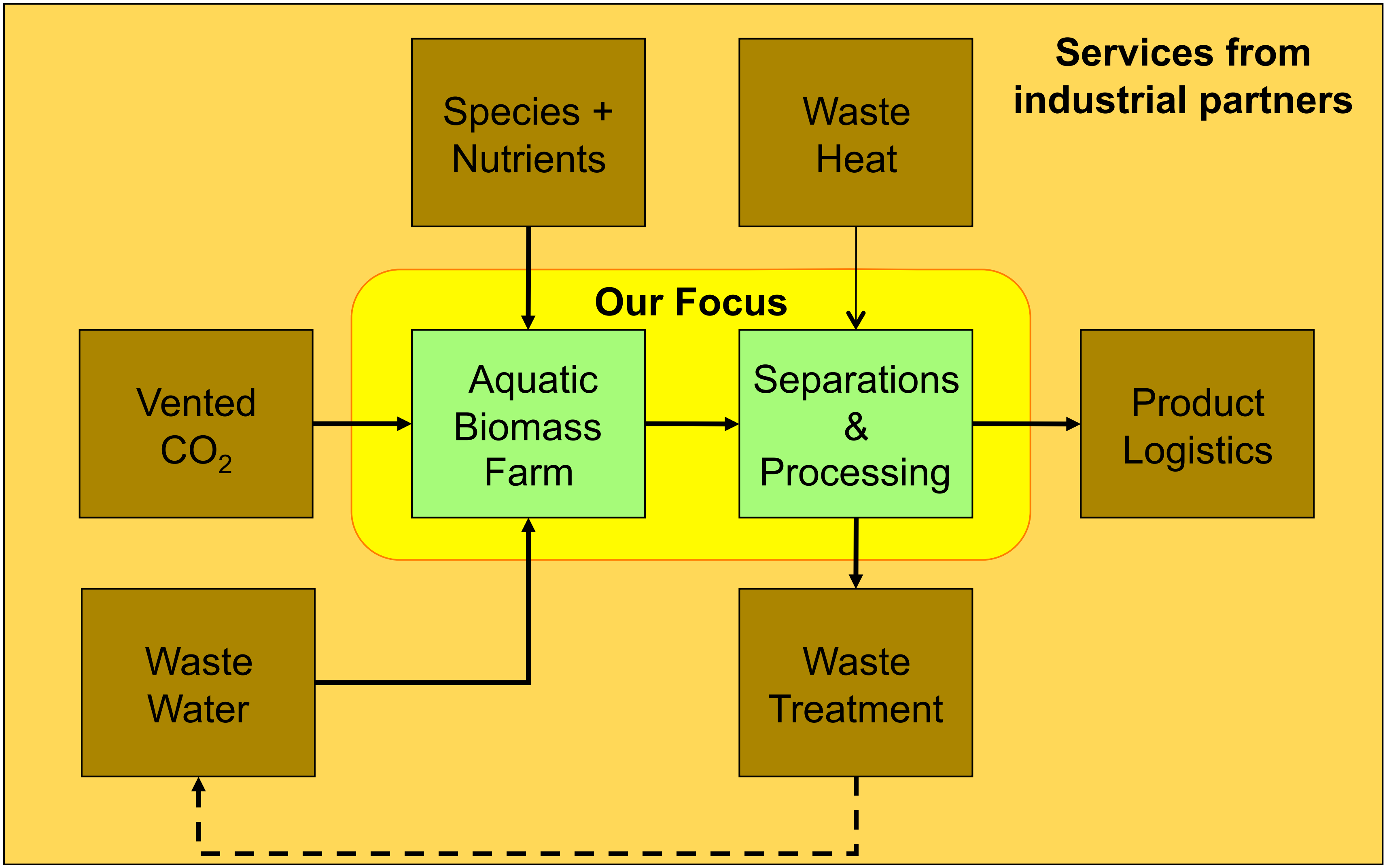
- The immense scale of fuel-growing precludes sterilization and exclusion of competing species



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



The feed market is not commensurate with the fuel market.

Sunrise Ridge

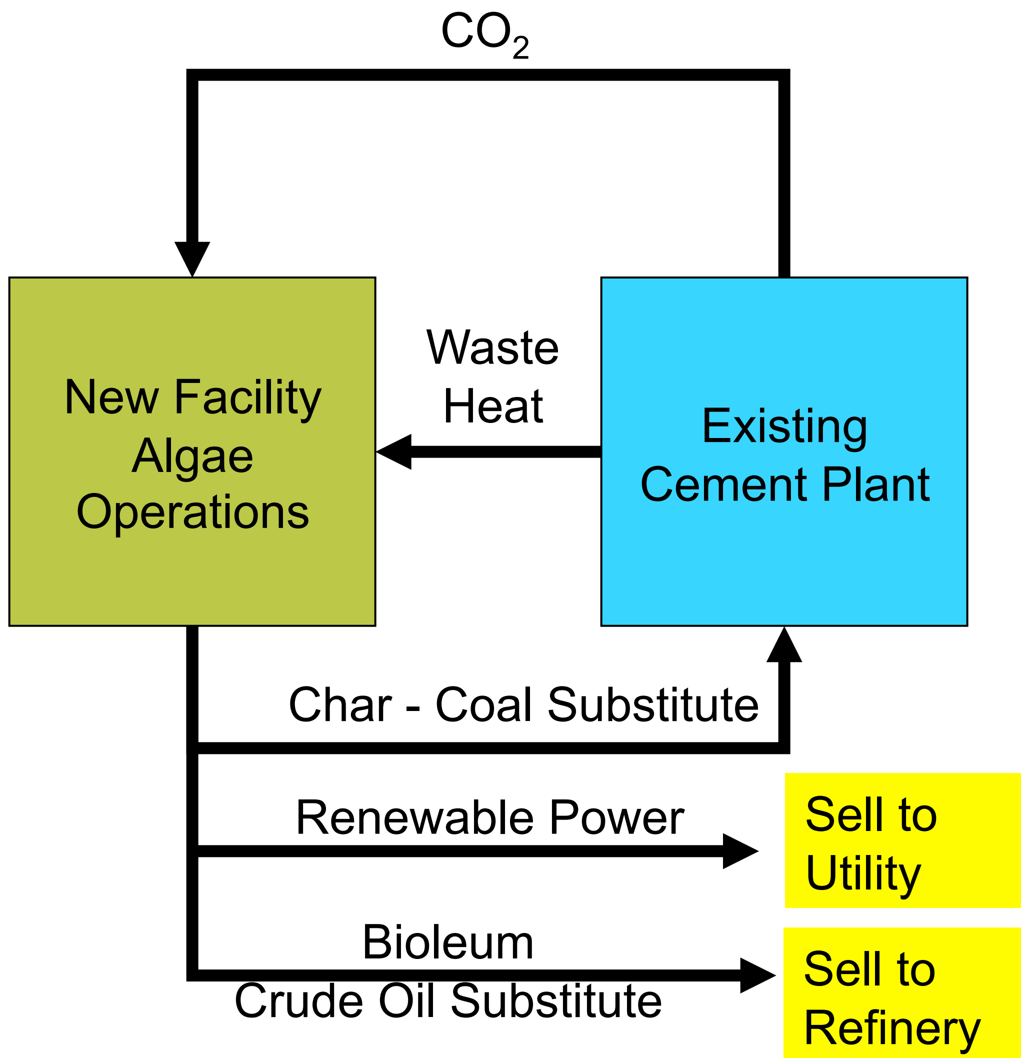
Material	Consumption rate in the US/T d^{-1}
Crude petroleum	3.2×10^6
Animal Protein forage (Pimentel)	8.8×10^5
Biomass-derived feed available if biomass (at 10% lipid yield) were used to provide 10% oil in US	2.9×10^5

"Food, Energy and Society" Pimentel & Pimentel 2008

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

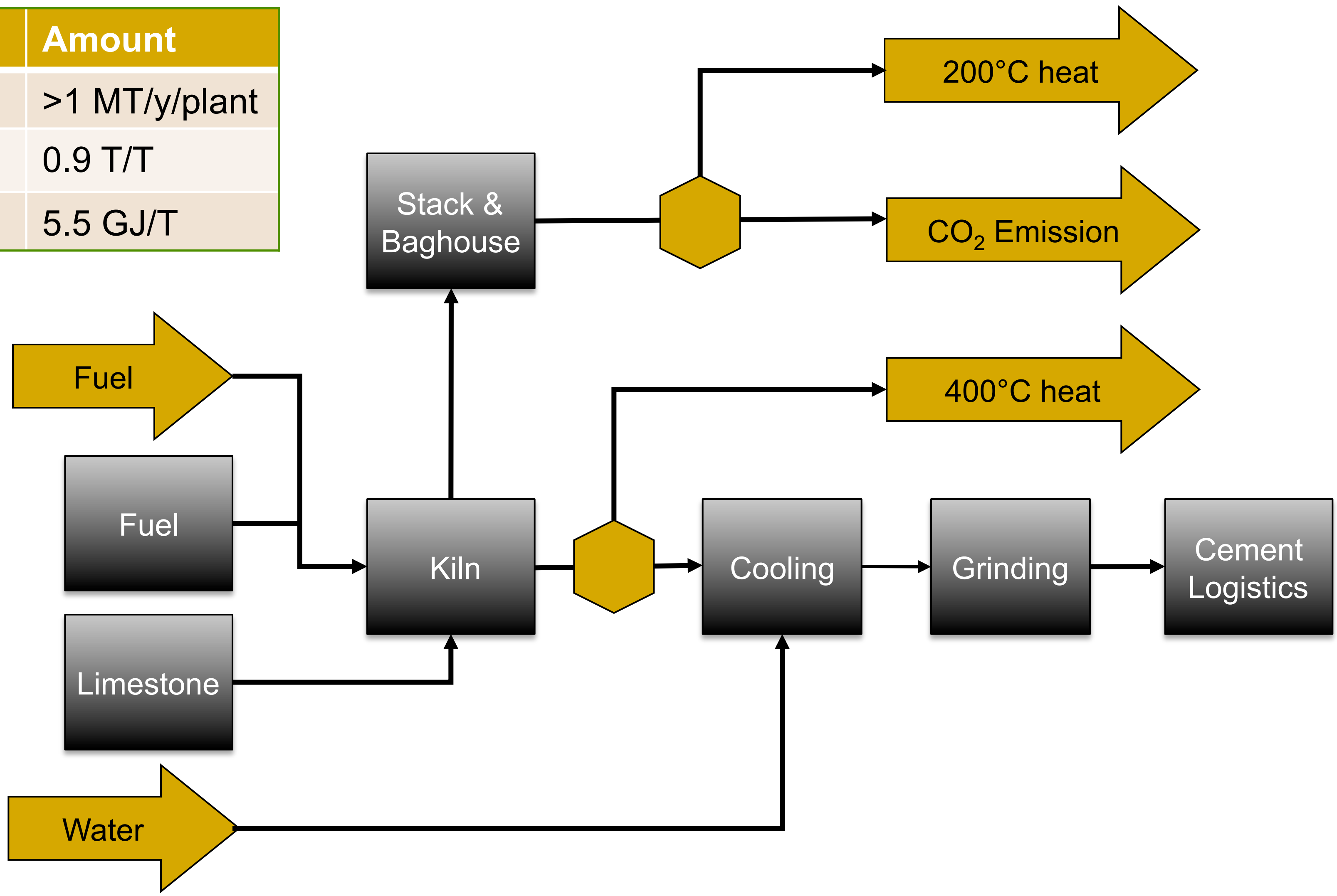
- Cement manufacturing creates about 0.9 T CO_2 per ton of cement along with copious quantities of waste heat.
- Cement sells for ~$90/T; CO_2 credits on the European market have ranged between €10-€35/T so inside-the-fence CO_2 offsets should be cost effective



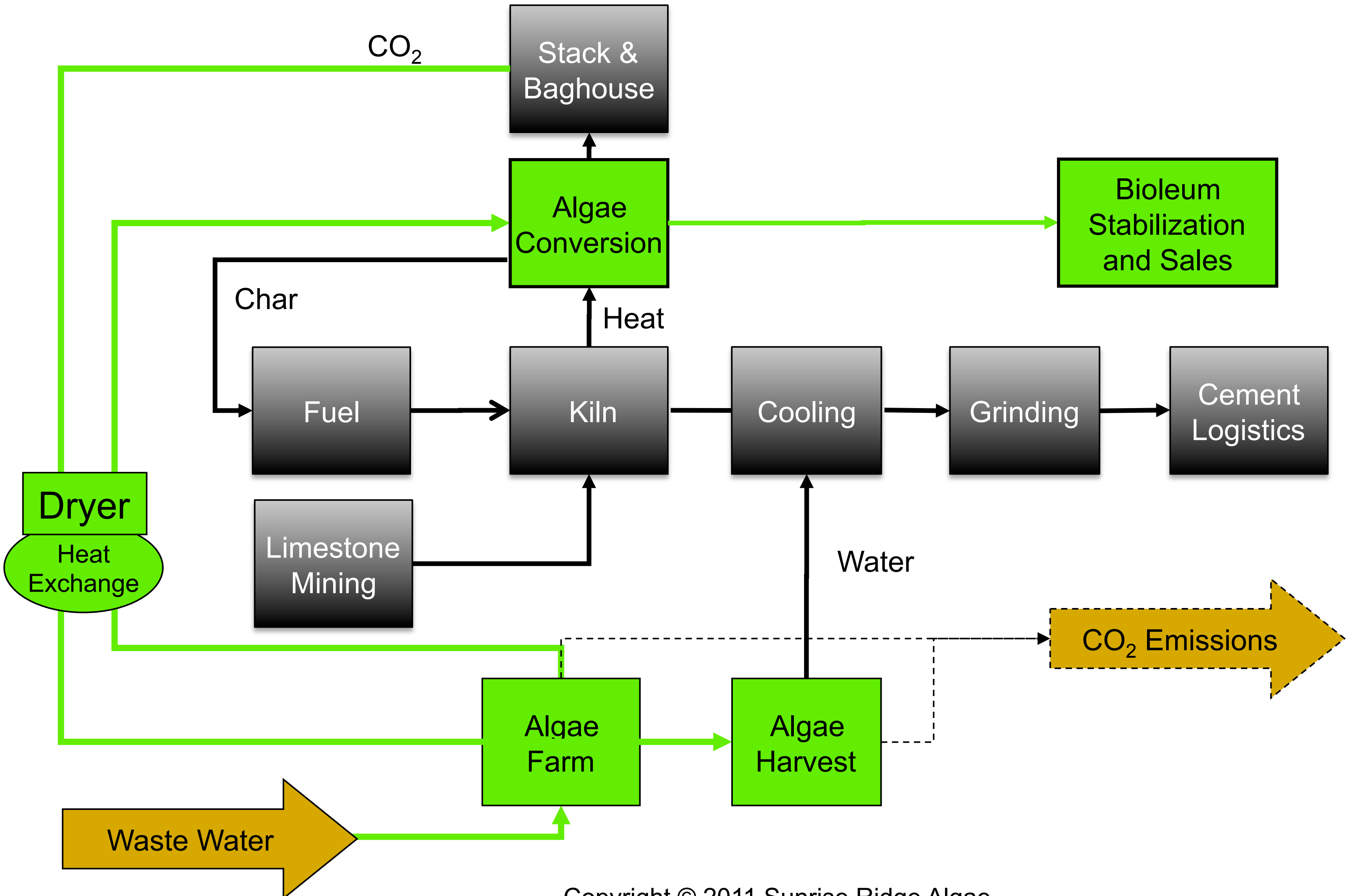
A cement plant has inputs and output streams that complement those of the production of renewable fuels.

Fun Facts about cement

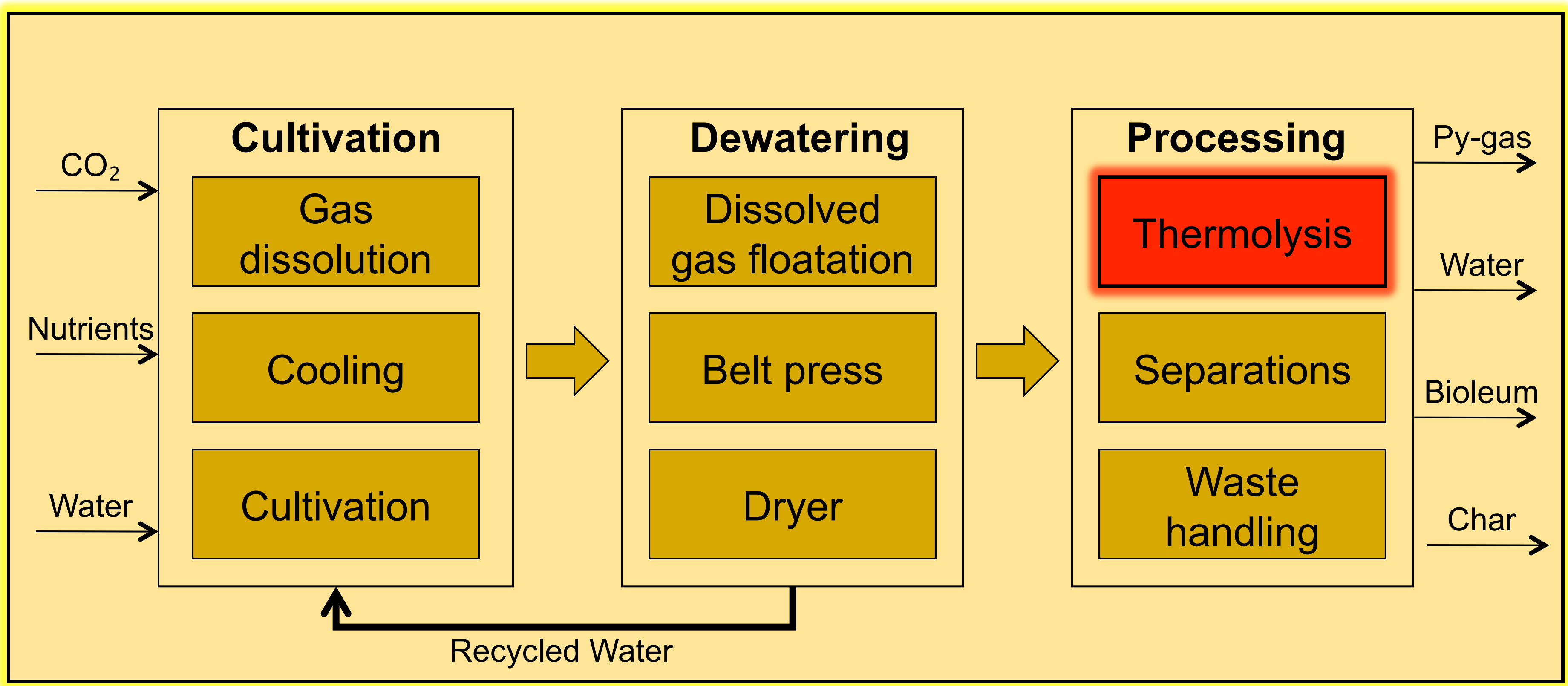
Stream	Amount
Cement	>1 MT/y/plant
CO_2	0.9 T/T
Fuel	5.5 GJ/T



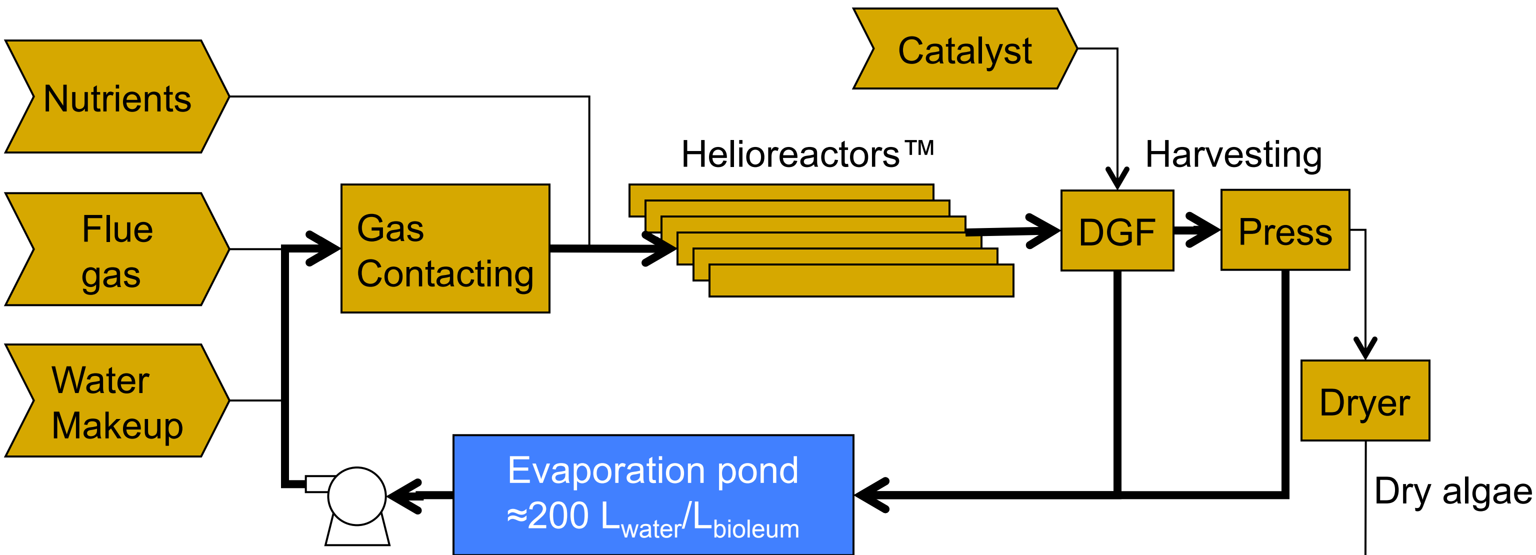
Our process took heat, CO_2 and water from the host site and returned water and fuel, minimizing emissions.



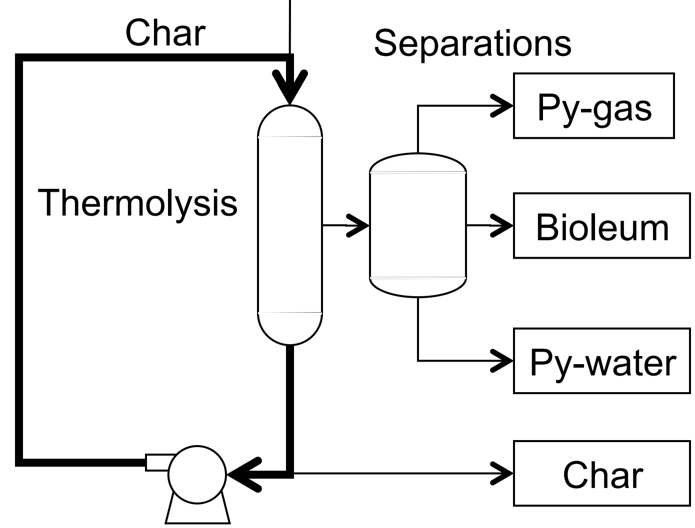
The process included three groups of algae operations: growth, harvesting and processing.



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

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

Aqueous flows for the 0.5 T/day design

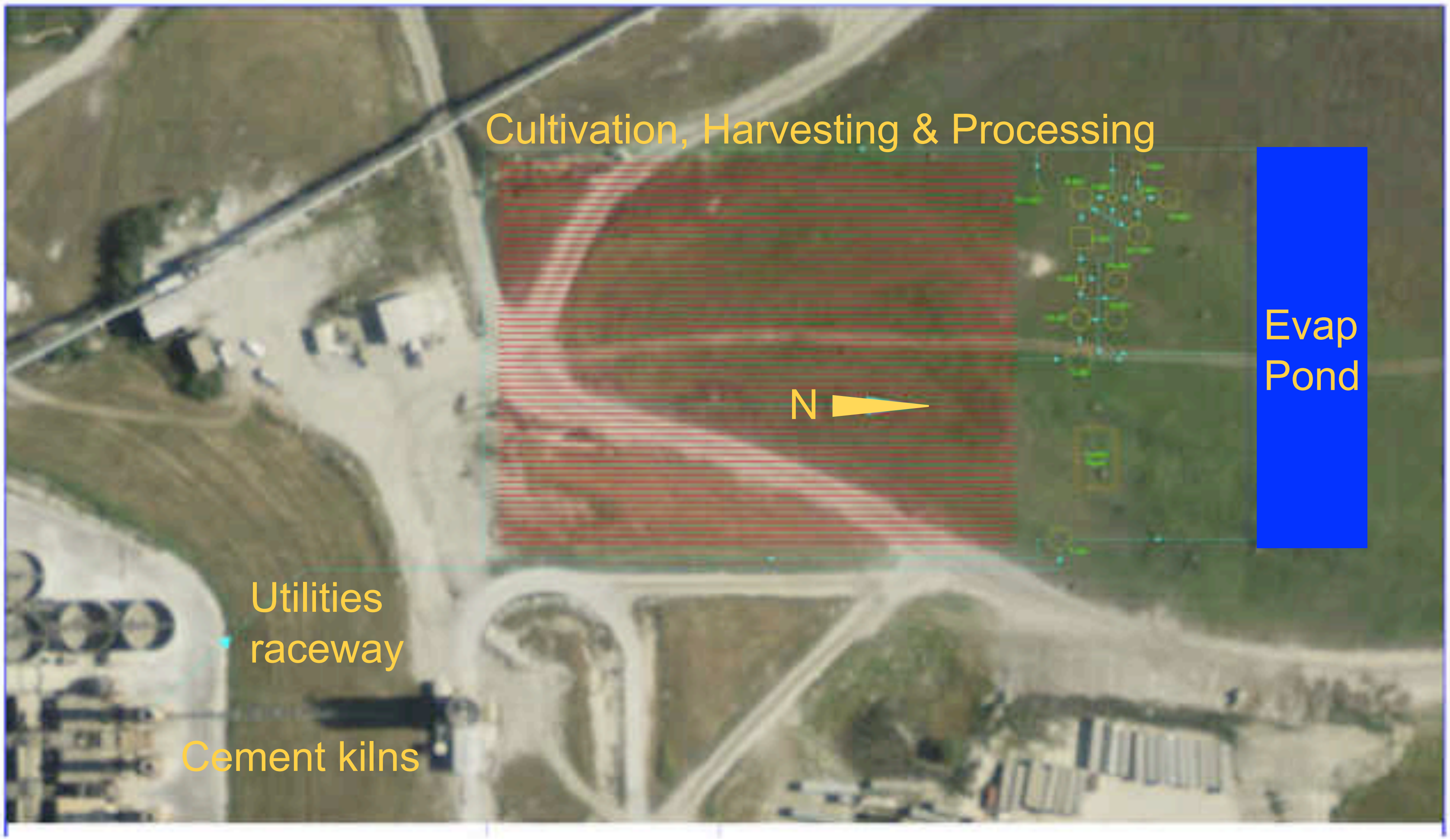
Input streams	Mass flows/kg h^{-1}	Output streams	Mass flows/kg h^{-1}
Flue gas	78	Helioreactor™ vent	5
Fertilizer	10	DGF vent	0
Makeup water	1,092	Dryer vent	18
Beltpress wash	200	Pond vent	1,045
		Blowdown	305
		Pywater+Pygas+flare	7
Total	1,380		1,380

All major units for the pilot plant was available commercially, had been tested at scale, or were project foci

Unit operation	Equipment	Status
Flue gas treatment	Gas washer, pumps compressors	Commercial
Water treatment	Mixers, nitrifiers	Commercial
Algae cultivation	SRA helioreactors	Tested at pilot scale
Algae harvesting	**Dissolved Gas Flotation; Belt press**	Commercial
Algae drying	Rotary dryer	Commercial
Thermolysis	Kiln, Condenser	Commercial, to be tested
Waste disposal	Flare,	Commercial
Power generation	Turbine gen set	Commercial

Site layout, pilot scale

At 0.5 T/day the algae cultivation, harvesting and processing could be sited on ~7 acres near the cement plant

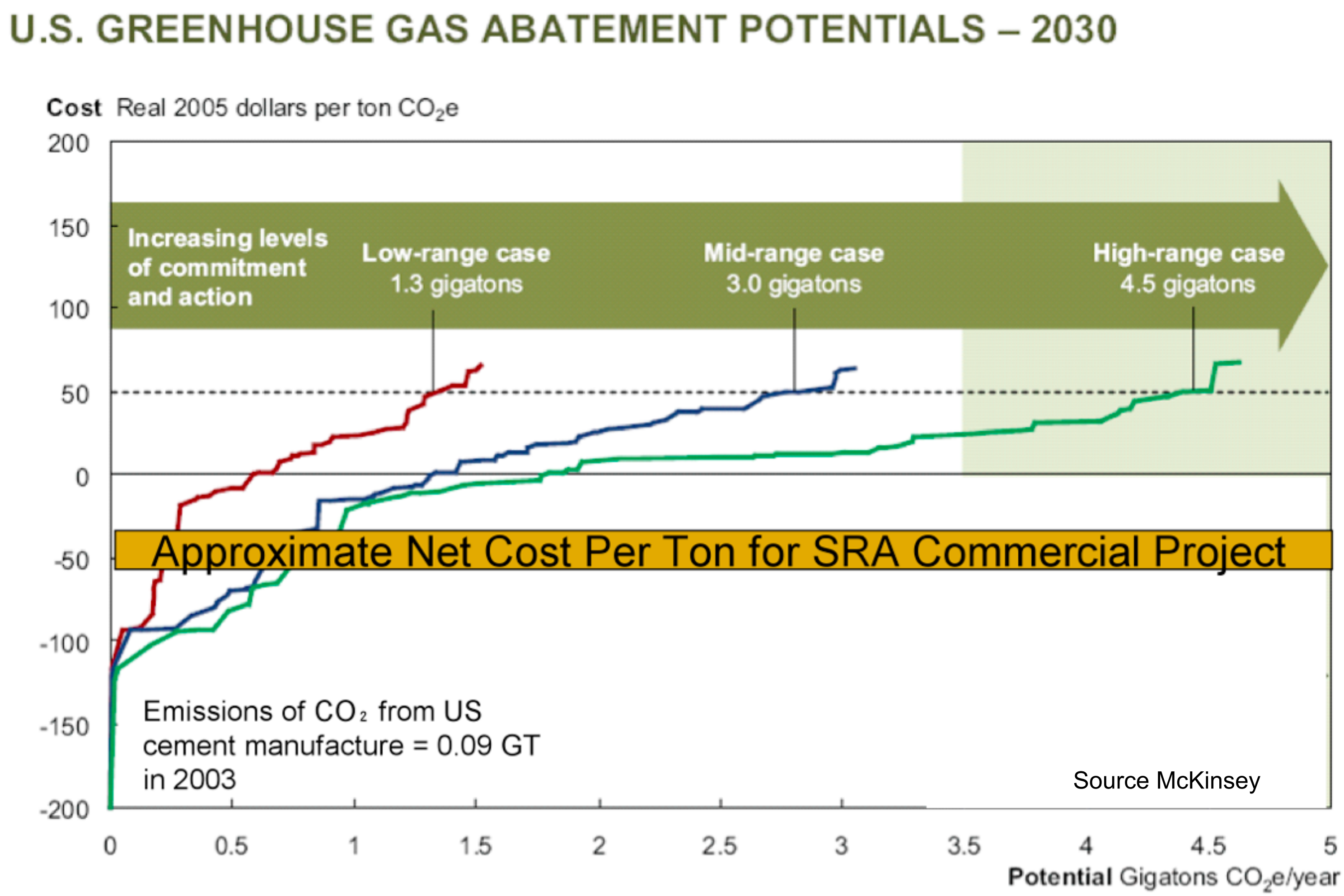


Beneficiating CO_2 via algaculture promised significant CO_2 savings…

Estimated lifecycle greenhouse gas emission reductions

Electricity source	Grid Power	Bioleum Gen Set			
Accounting method	**Co-Product Methods for bio-coal and Pygas**	**Allocation**	**Hybrid Substitution**		**U.S. Average Diesel**
	Life Cycle GHG Emissions (g CO_2e/MJ)				
CO_2 Uptake	-73.0	-73.0	-73.0	Crude Extraction	8.0
Electric power, combustion	13.1	0.075	0.2	Crude Transport	0.7
Oil Transport	0.4	0.4	0.4		
Refinery Co-processing	13.6	13.6	13.6	Crude Refining	8.8
Fuel T&D	0.6	0.6	0.6	Diesel T&D	0.5
Fuel Combustion	73.8	73.8	73.8	Fuel Combustion	74.8
Thermolysis Fuel Credit			-494		
Total (g CO_2e/MJ)	**28.5**	**15.5**	**-479**	**Total Fuel Cycle**	**92.8**
% Reduction from Petro-Diesel	**69.3%**	**83.4%**	**616%**	% Reduction from Petro-Diesel	0.0%

…as well as favorable economics compared to other approaches to CO_2 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:

$$\frac{1\times10^{6}T_{Cement}/y}{365day/y}\times\frac{0.9T_{CO_2}}{T_{cement}}\times0.7\frac{1T_{a\lg ae}}{1.8T_{CO_2}}$$

$$=960T_{a\lg ae}/day$$

$$\times0.25T_{bioleum}/T_{a\lg ae}\times6.1bbl/T=\boxed{1500bbl/day}$$

$$\times\frac{1day-m^{2}}{30\times10^{-6}T_{a\lg ae}}\times\frac{1hectare}{10^{4}m^{2}}=3200ha=\boxed{7700acre}$$

$$\times\frac{1L_{water}}{0.1\times10^{-6}T_{a\lg ae}}=9.6\times10^{9}L_{water}/day=\underbrace{\boxed{110\times10^{6}gal_{water}/h}}_{\text{circulation}}$$

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

Sunrise Ridge

Thermochemical upgrading can convert even low lipid biomass into bioleum, a high energy density crude.

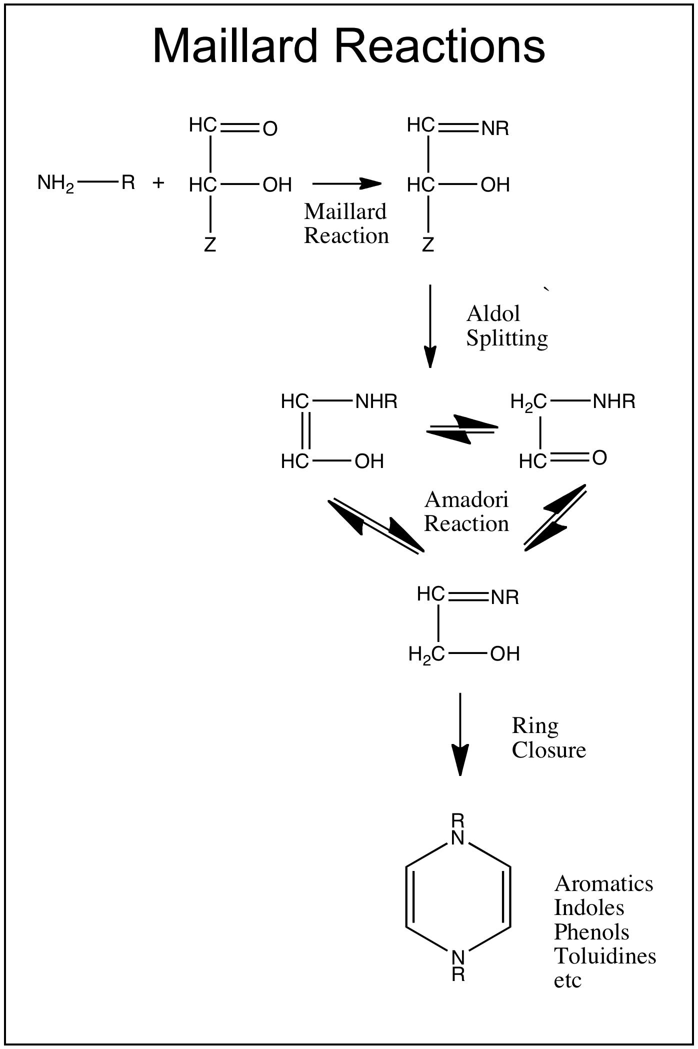
Characteristics of Bioleum

Material	HHV/MJ kg^{-1}
Crude petroleum	45-48
Jet fuel (minimum)	43
Refined biodiesel	38
Algae-derived bioleum	36
Cellulose-derived py-oil	13-18

- 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 H_2/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 and then via Amadori rearrangement products that eliminate oxygen as water.
- Use of a zeolite catalyst and CO_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 H2 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.

25 Sept 2009

26 Sept 2009

27 Sept 2009

- Lemnaceae (duckweed) include many native species
- They grow rapidly, doubling in about 1.5 day (algae can double twice per day)
- Like algae, they denutrify 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.

Feedstock	Areal yield bbl $h^{-1}y^{-1}$	"Blue" Water intensity[c] L L^{-1}
Vegetable oil *ex* soybeans	2[a]	6155
Pyrolysis oil *ex* wood	2[b]	2600
Algae[d]	300	200 est
Bioleum *ex* lemna (est.)[e]	60	–400 est

a) Eestimated from yield published in http://www.ces.purdue.edu/extmedia/ID/ID-337.pdf
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
c) Irrigation water; W. Gerbens-Leenes, AY. Hoekstra and T. H. van der Meer, Proc. Nat. Acad. Sci., 2009, www.pnas.org/cgi/doi/10.1073/pnas.0812619106
d) Weyer, et al., Theoretical maximum algal oil production, Bioenergy Research, 2009, DOI 10.1007/s12155-009-9046-x
e) assumes treatment that permits total recycle of the growing water omits evaporative "green" water F. A. Agblevor and S. Besler-Guran, *Fuel Chemistry Division Preprints* ***2002****, 47(1), 374;*

Fluid	US consumption/L day^{-1}
Petroleum (20 million bbl/day)	10
Water (410 Bgal/day)	5000

So, replacement of ~10% of the US fuel supply with fuels derived from soybeans or wood could significantly increase water usage.

To summarize:

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 CO_2 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.

Sunrise Ridge

- **Funding**: DOE/NETL
  Texas Emerging Technology Fund
- **SRA**: Norm Whitton, David Griffith, Sara Norris, Josh Morgan
- **Life Cycle Associates**: Stefan Unnasch
- **URS Corporation**: *inter alia* Carl Richardson, Doug Orr, Dennis Dalrymple, Tommy Bell, Craig Holloway, August Martin, Susan Ferguson, and Glenn Dewolfe (deceased)
- **A cement company in central Texas**