

Mechanical Engineering

Fuel from Algae?

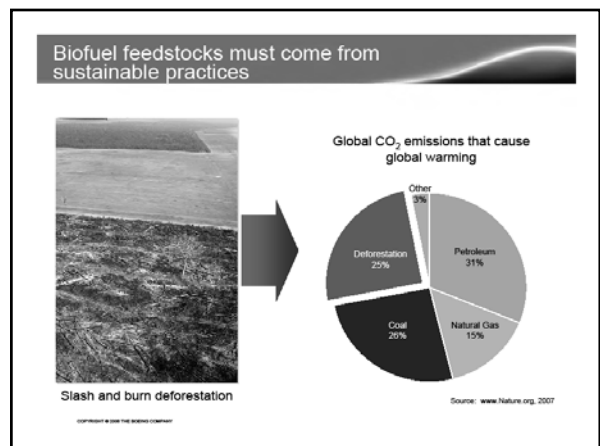
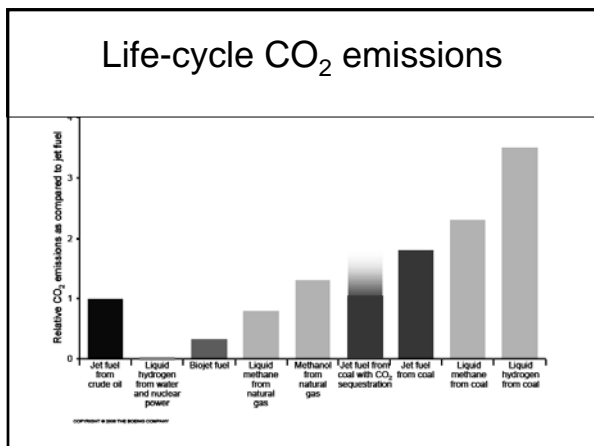
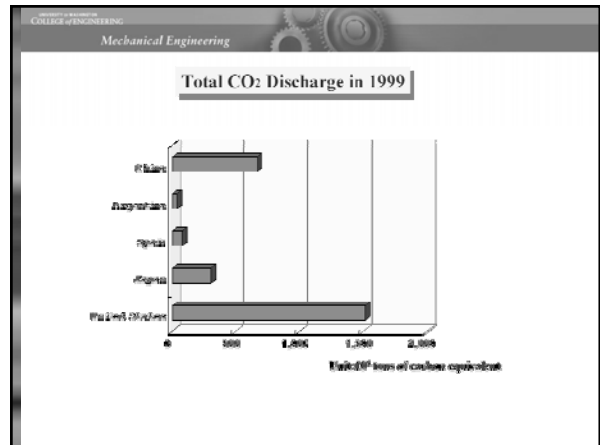
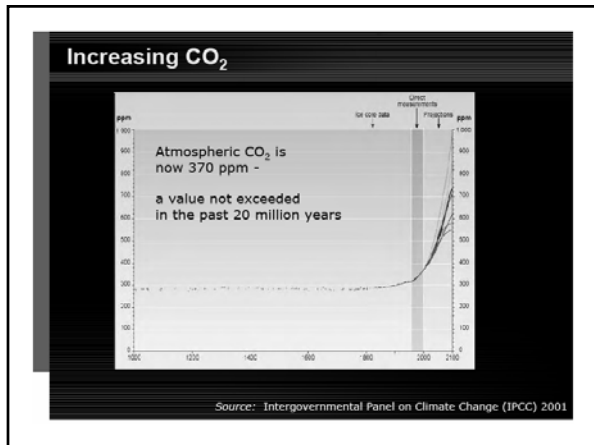
A. Mescher, J. Kramlich

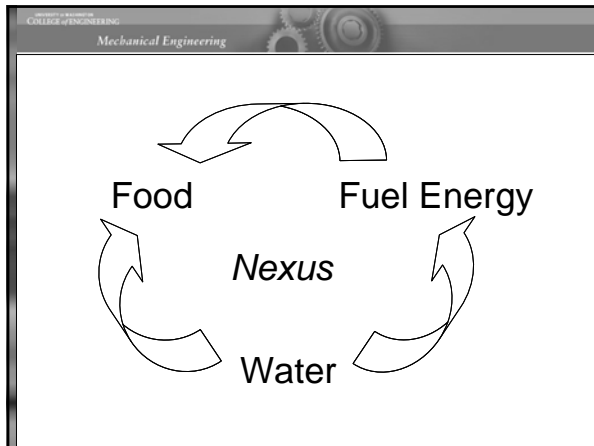
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Fuel market and emissions

- U.S. Transportation: 180 billion gallons fuel per year.
- Europe: 5.75% bio-diesel content by 2010, 10% by 2020.
- Majority of industrialized world signed Kyoto Treaty to reduce greenhouse gas emissions.
- President elect Obama sets goal of 1990 level emissions by 2020.





450 pounds of corn = 1 SUV Tank = Enough calories to feed one person for a year

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Vast Areas of the Globe Are Not Suitable for High Levels of Terrestrial Agriculture

Atlas of the Biosphere
But could be used for algal culture.

Energy and Agriculture withdraw the most water in the U.S.

U.S. Freshwater Withdrawals - 340 Billion gallons/day (in 2000)
Estimated Freshwater Withdrawals by Sector, 2000

Sector	Percentage
Thermoelectric	39%
Irrigation	35%
Public Supply	14%
Primarily Nonconsumptive	10%
Primarily Consumptive	10%
Livestock	2%
Industrial	0%

Note: Hydropower and saline water uses are not included here!

Water challenges are nationwide

Projected Population Growth (1995-2025)

Legend for Water Challenges:

- High water demand
- Low water
- High water
- High water demand

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Resource Requirement: Water

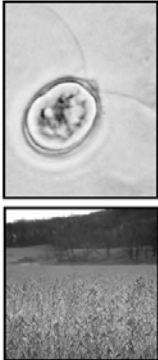
Saline aquifers in the U.S.

- Water with few competing uses
- Water resources show many areas of intersection with cheap land and CO₂ sources
- "Produced water" from oil wells potential source
- Seawater available in many parts of the world
- Identify ideal sites with more recent information

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Why Algae?


- Much greater productivity than their terrestrial cousins
- Non-food resource
- Use otherwise non-productive land
- Can utilize saline water
- Can utilize waste CO₂ streams
- Can be used in conjunction with waste water treatment
- An algal biorefinery could produce oils, protein, and carbohydrates



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Comparing Potential Oil Yields

Crop	Oil Yield Gallons/acre
Corn	18
Cotton	35
Soybean	48
Mustard seed	61
Sunflower	102
Rapeseed/Canola	127
Jatropha	202
Oil palm	635
Algae (10 g/m ² /day at 15% TAG)	1,200
Algae (50 g/m ² /day at 50% TAG)	10,000




Fatty acid composition of algal oils suitable for preparation of biodiesel

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Why Algae in Washington?

Waste Water Pond



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Agro-Human Marine Pollution



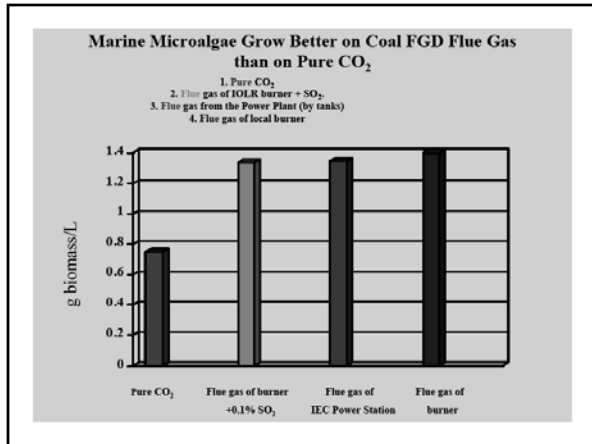
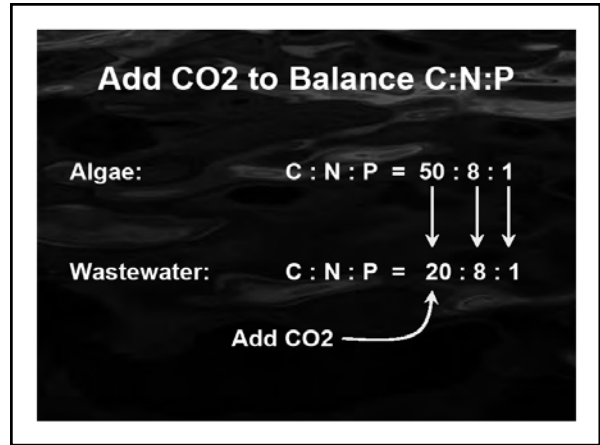
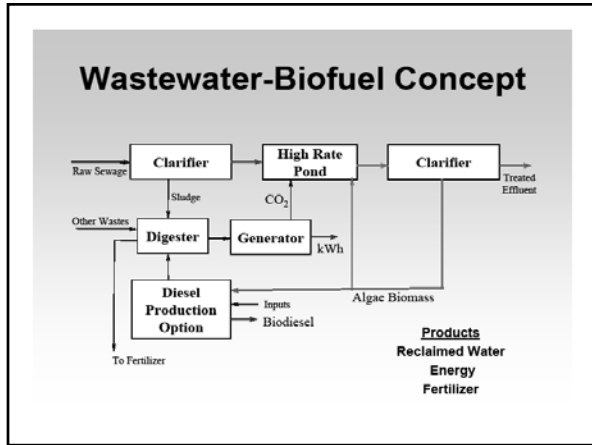
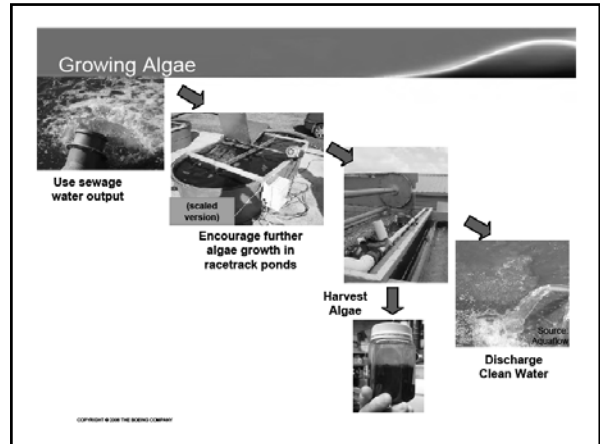
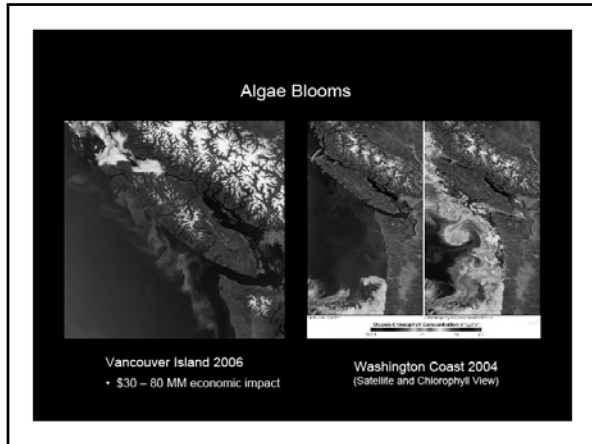
The Conditions that Lead to Algae Blooms

- Nutrients (Agricultural and Human Runoff)
 - Phosphorus
 - Nitrogen
- Dissolved Carbon Dioxide in Water system:



Factors that enhance Algae Blooms

- Population Growth = Increased Nutrients
- Increase CO₂ = Faster Algae Growth
- Increased Water Temperature = Faster Algae Growth



Numerical Example: Algal Raceway Simulation

Hydrodynamics

- EFDC solves vertically hydrostatic momentum and continuity equations for turbulent flow
- Withdrift/return BC simulates a paddlewheel
- When properly configured, solution stabilizes quickly
- Explicit numerical solution yields problems amenable for solution on Georgia's large computing clusters

Atmospheric Forcing

- Considered one year of input data for Palm Springs, CA, 2005
- Monthly observations of the following:
 - Insolation radiation
 - Temperature
 - Cloud cover
 - Evaporation
 - Precipitation
 - Relative humidity
 - Atmospheric pressure
 - Wind speed
 - Cloud cover

Algal Growth Model

- Algal growth kinetics are based on US Army Corp of Engineers CE-QUAL model
- Includes solar radiation, nutrient availability, predation, temperature, respiration, etc.

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Cost of Algae Production

1982 - Benemann *et al.* created one of the least expensive production systems – using open ponds - the cost of algae produced was around 40 to 50 cents/kg in today's dollars.

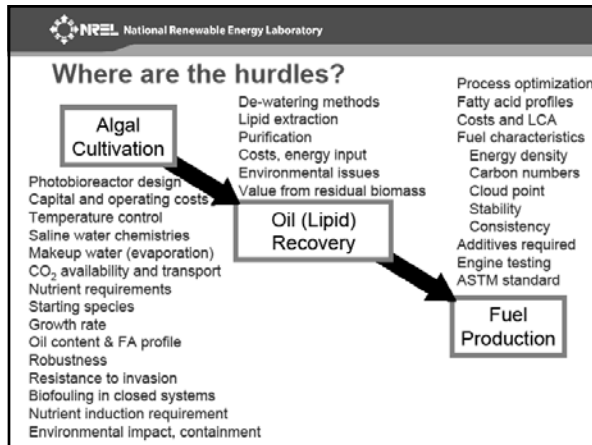
1988 - Tapie & Bernard used tubular bioreactors at a cost of \$9 to \$10/kg.

1992 - Coutteau & Sorgeloos observed a cost > \$600/kg using plastic bags and other closed systems.

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Value of Algal Oil

- At 30% lipid content, 10 kg algae yields 3 kg oil ~ 1 gallon
- For comparison, petro-oil value ~ \$3 per gallon
- Value of dry algae ~ \$3 / 10 kg = 30 cents per kilogram



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Some benchmarking

High β-carotene-algal Productivity at Minimum Cost



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Spirulina


Harvest densities
1:3000

This could be lots of work!

Annual Microalgae Production Costs NBT <i>Dunaliella</i> Plant versus Alternative Bio-Fuel Algal Plant (10 Hectares Plant Open Ponds)		
	<i>Dunaliella</i> NBT Ltd., Eilat, 2006	Alternative Algal Plant 2007
Cost in US\$/year		
Manpower	500,000 (20 workers)	?
Electricity (\$0.125/KW)	100,000	?
Fertilizers (N,P,K, Fe) and other chemicals	30,000	?
Domestic Land City Taxes	50,000	?
CO ₂ (\$400/ton)	150,000	?
Sea Water (\$0.25/m ³)	200,000	?
Fresh Water	20,000	?
Other supplies and Miscellaneous	30,000	?
Total	1,165,000	?
Yearly production of dry algae biomass	70 tons (2g/m ² .day)	?
Cost of 1Kg dry microalgae	\$17.00/kg	\$0.34/kg ???
Market Price	\$4,000/kg algal AFDA (B. Carotene Health Food) Total sale ~\$US 200 million/year	Algae cost for bio-fuel should be below \$0.5/kg algal AFDW

Major Production Costs:
NBT Ltd. Eilat
Super Centrifuge ~ \$750,000
(Westfalia, Germany)
High Electric Running Cost (24hrs/day)

Production Cost
Manpower
Electricity (\$0.125/KW)
Fertilizers (N,P,K, Fe) and other chemicals
Domestic Land City Taxes
CO ₂ (\$400/ton)
Sea Water (\$0.25/m ³)
Fresh Water
Other supplies and Miscellaneous
Total
Yearly production of dry algae biomass
Cost of 1Kg dry microalgae



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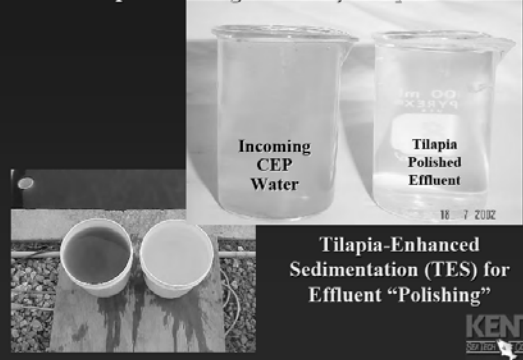
Electric costs for centrifuging: \$2.60 per kg

Ugh! ?

Drying?

Filtering?

Uptake of Algal Cells by Tilapia


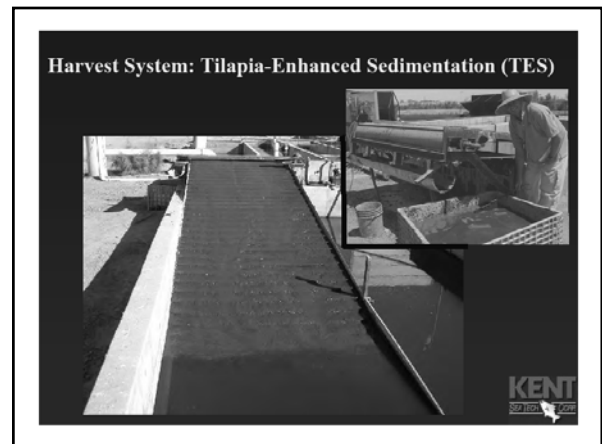
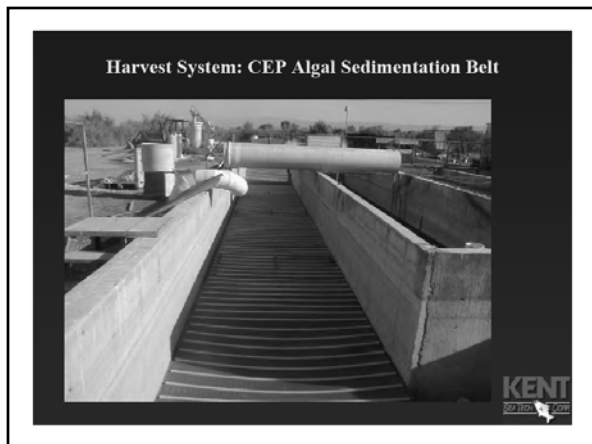


Incoming CEP Water

Tilapia Polished Effluent

18 - 7 2002

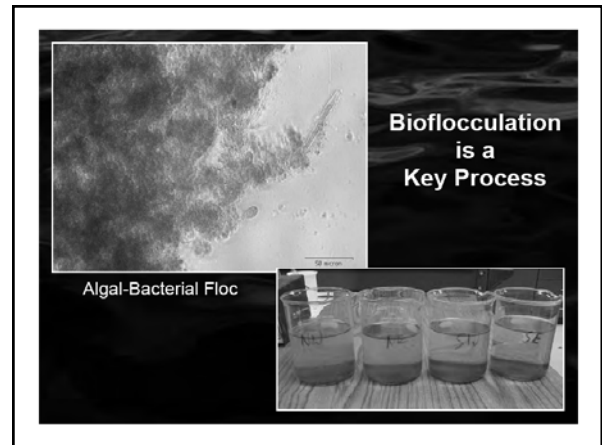
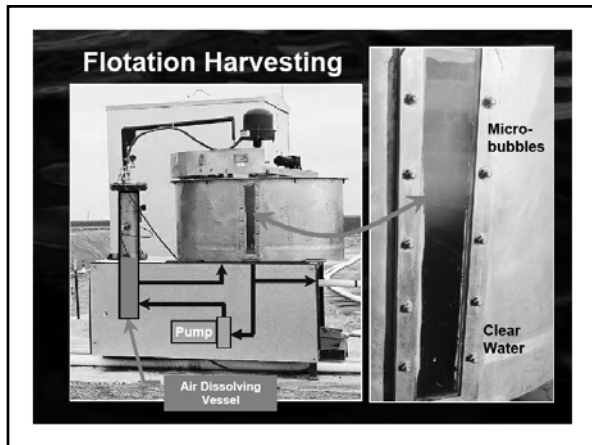
Tilapia-Enhanced Sedimentation (TES) for Effluent "Polishing"



Chemical Coagulation & Dissolved Air Flotation

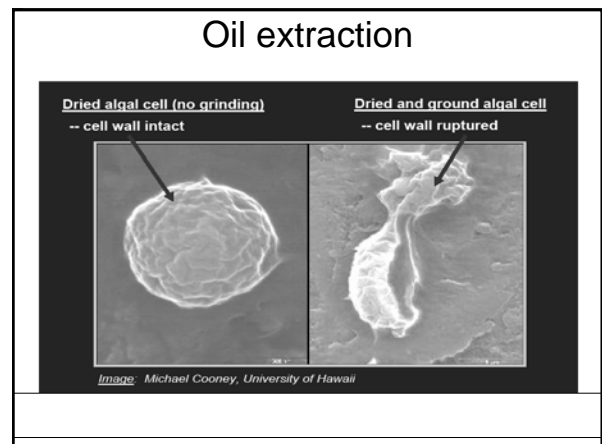
- **Metal Salts & Petroleum-based Polymers**
 - Creates algae flocs
 - \$300 to \$600 per MG to meet nutrient limits
vs. \$310 per MG median US WWT cost (2002, AMSA)
- **Dissolved Air Flotation**
 - Mechanical floc removal
 - Pressurized air and water

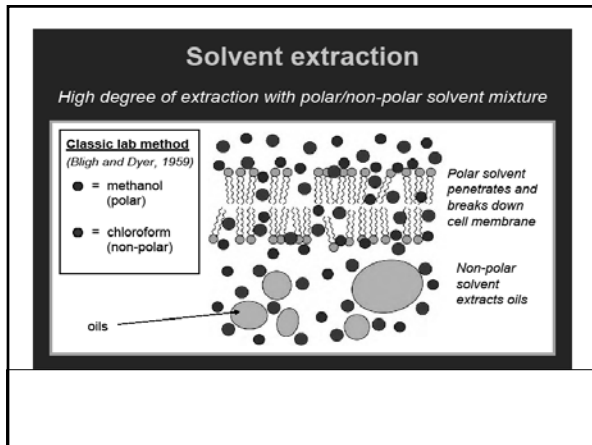
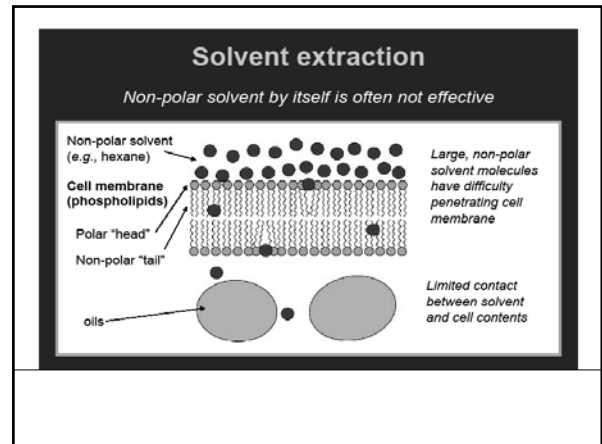
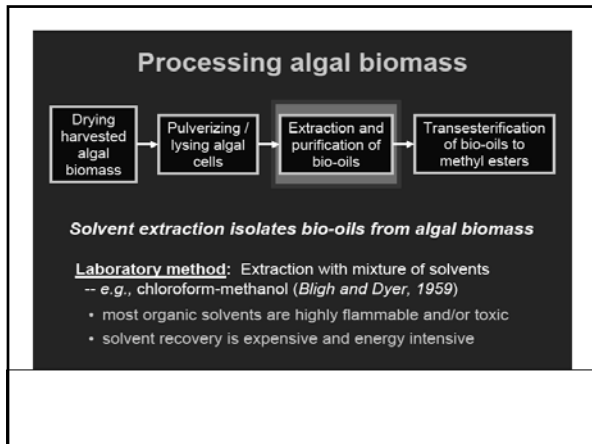


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Critical Challenges

- **Algal strains for high-level production**
 - Fast growth
 - High oil production
 - Resistance to contamination
- **Cultivation facility design**
 - High vs. low intensity
 - Water sources
 - Nutrient sources
 - Harvesting
- **Conversion to fuel and other products**





Supercritical Fluids in Industry

- Reactions
 - SC Water Oxidation
 - Catalysis
- Pharmaceuticals
 - Particle Formulation
 - Drug Delivery
- Extraction
 - Petroleum
 - Coffee Decaffeination
 - Essential Oils

<http://www.expsep.co.uk/>

Experimental Apparatus

- Supercritical Fluid Technologies
- SFT-150
 - LED Temperature display/controller
 - Precision: $\pm 0.5^\circ\text{C}$
 - Max Vessel Temperature: 300°C
 - Max Operating Pressure: 680atm
 - Max Flowrate: 250g/min CO_2
 - Rupture disc safeguard
 - External Collection Vessel
 - Hand-tight vessel seals

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In our lab:

Hexane solvent extraction using Soxhlet apparatus

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Cost for Supercritical Extraction?

- Comparison of cost for hexane solvent extraction versus supercritical CO₂
- Supercritical CO₂ less expensive but at \$2 per lb or about \$5 per kilogram

Ugh!

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Boeing Sponsored Project


- Interest in Biojet fuel
- Study fuel oil yield and composition (molecular weight and distribution) depending on processing conditions and methods.

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Fuel Properties Depend on Chain Length

- Viscosity, surface tension ---> Atomization
- Freezing temperature --> Wing tanks
- Flammability limits, quenching limits, flame speed --> Compatibility with existing combustors

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Soxhlet apparatus periodically immerses the sample in solvent during each solvent exchange, or "reflux," which allows us to extract varying mass fractions of the sample's total lipid content.

Small aliquots of combined solvent and extracted lipid are removed, after a specified number of solvent refluxes. The number of solvent refluxes is directly proportional to the period of time over which the algal sample is immersed in the solvent. As the number of refluxes increases, so also increases the extracted mass percentage of the alga's total lipid content.

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Oil Structure

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{H} - \text{C} - \text{O} - \text{C} \begin{array}{l} \text{O} \\ || \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array} \\
 | \\
 \text{H} - \text{C} - \text{O} - \text{C} \begin{array}{l} \text{O} \\ || \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array} \\
 | \\
 \text{H} - \text{C} - \text{O} - \text{C} \begin{array}{l} \text{O} \\ || \\ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \end{array} \\
 | \\
 \text{H}
 \end{array}$$

Fats are glycerin molecules with carboxylic acid chains attached

Length can be 8-22 carbons. Can be unsaturated. Goal for biojet is 8-16, while algae produces through 22.

Raw fats not suitable for jet fuel (too viscous, etc.)

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Refined by Transesterification

$$\begin{array}{c}
 \text{H} \\
 | \\
 \text{H} - \text{C} - \text{O} - \text{C} \begin{array}{l} \text{O} \\ || \\ \text{R}_1 \end{array} \\
 | \\
 \text{H} - \text{C} - \text{O} - \text{C} \begin{array}{l} \text{O} \\ || \\ \text{R}_2 \end{array} \\
 | \\
 \text{H} - \text{C} - \text{O} - \text{C} \begin{array}{l} \text{O} \\ || \\ \text{R}_3 \end{array} \\
 | \\
 \text{H}
 \end{array}
 + \text{CH}_3 - \text{OH} \rightarrow \begin{array}{c} \text{O} \\ || \\ \text{CH}_3 - \text{O} - \text{C} - \text{R}_1 \\ \text{O} \\ || \\ \text{CH}_3 - \text{O} - \text{C} - \text{R}_2 \\ \text{O} \\ || \\ \text{CH}_3 - \text{O} - \text{C} - \text{R}_3 \end{array} + \begin{array}{c} \text{H} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{H} \end{array}$$

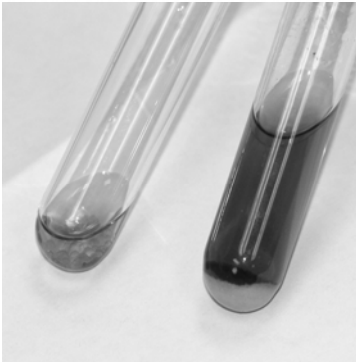
Fat treated with alcohol and acid or base catalyst

Produces two phases: biofuel and glycerin (containing wastes)

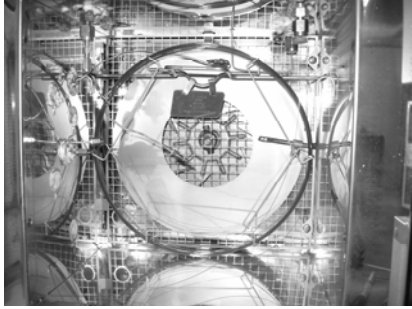
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Transesterification procedure is an adaptation of AOCS method Ce-89b.

Transesterified product (left) and glycerol / salt solution (right).



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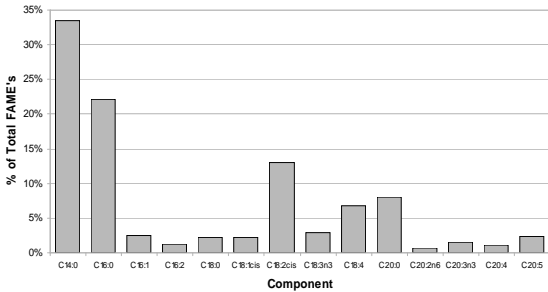
Capillary column of Gas Chromatography System

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Machine: PerkinElmer Autosystem XL with capillary injector and FID using a Supelco fused-silica SPB-PUFA column (30m length by 0.32mm i.d., 0.2µm film).

Temperature program: 240°C injection in a PerkinElmer capillary injector with a 30 second splitless period followed by 50:1 split. Initial 80°C column temperature with a 1 minute hold, followed by a ramp of 10°C per minute to 210°C at 14 minutes, with a hold at 210°C until 40 minutes. FID at 260°C.

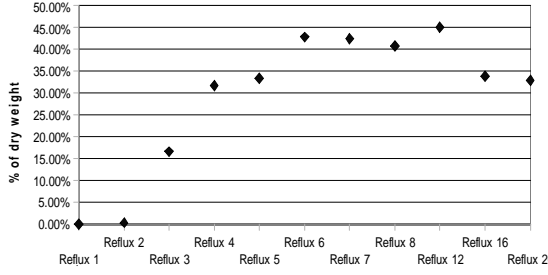
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Component	% of Total FAME's
C10	33.0
C16	22.0
C18:1	3.0
C18:2	1.5
C18	2.5
C18:1n-6	2.5
C18:2n-6	13.0
C18:3n-3	3.0
C18:4	6.5
C20	8.0
C20:2n-6	1.0
C20:3n-3	1.5
C20:4	1.5
C20:5	2.5

Relative Lipid Content, % mass basis

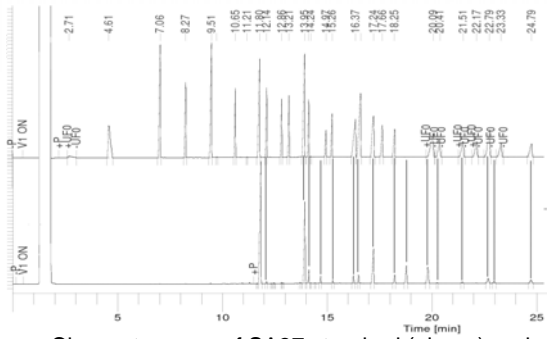
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Reflux Number	% of dry weight
1	0.00
2	0.00
3	16.00
4	32.00
5	34.00
6	43.00
7	42.00
8	41.00
12	45.00
16	35.00
20	33.00

Extracted FAME mass (percentage of dry algal mass) as a function of reflux number

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Chromatograms of SA37 standard (above) and transesterified lipids (below).

For us, it's all about

Energy Costs of Processing!

- Dewatering
- Extraction
- Transesterification or ?
 - Alcohol needed
 - Mechanical work or heating needed
 - Glycerol byproduct?
- Fuel cleaning/catalyst removal
- Goal: Get needed composition with economically optimum yields and low energy costs