Algae
A Renewable Energy Source

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Outline

- Types of algae
- Growth requirements
  - Open pond vs. bioreactor
- History of research
  - NREL – Aquatic Species Program
- Fuel types
- Advantages / disadvantages
- Other uses (co-products)
- Current initiatives
Types of Algae

- **Macroalgae**
  - Freshwater and marine plants - “seaweeds”
  - Fast growing
  - Can grow upwards of 60 m in length

- **Emergents**
  - Aquatic plants that grow partially submerged in bogs and marshes
Types of Algae

- **Diatoms** (Bacillariophyceae)
  - ~100,000 species
  - Marine, brackish, or fresh water
  - Cell walls contain polymerized silica
  - Store carbon as oils or chyrsolaminarin (polymerized carbohydrates)
Types of Algae

- Green algae (Chlorophyceae)
  - Freshwater
  - Single cell or colonies
  - Stores carbon as starch
    - Can produce oil under certain conditions
Types of Algae

- **Blue-green algae (Cyanophyceae)**
  - Similar to bacteria
  - ~2,000 species
  - Important to nitrogen fixation

- **Golden algae (Chrysophyceae)**
  - Similar to diatoms (color / biochemistry)
  - ~1,000 species
  - Primarily freshwater
  - Store carbon as natural oils and carbohydrates
Growth Requirements

- Sunlight
- Water
- CO₂
- Minerals / nutrients

Diagram:
- Minerals (N, P, K, Mg, Na, S, Trace metals)
- H₂O
- CO₂
- Light
- Organic substrate
- Biomass
Open Pond Systems

- **Pros**
  - Most economical method
  - Larger growth area
  - Use co-located power plant or sewage plant for \( \text{CO}_2 \) and nutrients

- **Cons**
  - Temperature dependant on location
  - Local species work best
  - Difficult to grow monocultures
  - Rainfall / evaporation can change salinity and pH
Bioreactors

- **Pros**
  - Can control nutrient level, pH, salinity, light intensity, and CO₂ levels
  - Can be used anywhere (doesn’t compete with farmland for food)
  - Can grow single colonies, not dependant on surrounding environment
- **Cons**
  - Expensive!
Other Growth Systems

- Greenhouse systems
  - Plastic or glass tubes
  - Polyethylene bags
  - Covered raceway ponds
- Wind farm / seaweed farm
History of Research

- National renewable Energy Laboratory (NERL)
  - Aquatic Species Program (ASP)
    - 1978 to 1996
    - Department of Energy program to develop renewable transportation fuels from algae
    - Funded by DoE Office of Fuels Development
Aquatic Species Program

- Collected and studied over 3,000 algal strains
- Algae good source of fuel energy
- Can produce up to 30 times more oil than terrestrial oilseed crops
  - 200,000 hectares (less than 0.1% suitable land area in U.S.) could supply one quad of fuel
    - 1 quad = $10^{15}$ Btu of energy (1 Btu $\sim$ 1kJ)
  - Provide more energy than current oilseed crops
- Biodiesel cost at least twice that of petroleum diesel fuel (1998)
Aquatic Species Program

- 1978 to 1982
  - Focused mainly on production of hydrogen from algae
  - Switched focus to biodiesel in early 1980’s
- Unable to find one strain that exhibited optimal properties (rapid growth, high lipid production, high constitution)
Aquatic Species Program

- **Focus on microalgae**
  - *Diatoms*
    - Main storage compound lipid
    - Can increase lipid production by Si deprivation
      - This also decreased the overall biomass production
  - **Green algae**
    - Starch as primary storage
    - Can promote lipid accumulation by N deprivation
  - **Golden-Brown algae**
    - Lipid primary storage
- **Green algae and diatoms best candidates**
Aquatic Species Program

- Focused on southwestern United States as potential “farm” land
  - Brackish water
  - Climate
  - Non-arable land
Aquatic Species Program

- Focused on open pond raceway systems
  - Depth of pond
  - Pond circulation
    - Paddle wheel
    - Air lifters
  - Harvesting methods
    - Filtration
    - Flocculation
    - settling
Aquatic Species Program

- 1980 – 1987 Algal Raceway Production System (ARPS)
  - Operated in Hawaii
  - Used airlift system for water circulation

- 1981 – 1986 High Rate Pond (HRP)
  - Operated in California
  - 8 month growing season
  - Achieved 15 – 20 g/m²/day
  - Continuous operation ~ 20% more efficient

- 1988 – 1990 Outdoor Test Facility (OTF)
  - Operated in Roswell, NM
  - Average overall productivity ~ 10 g/m²/day
  - Target ~ 50 g/m²/day
Aquatic Species Program

- Program goals (to be economically viable)
  - 18% photosynthetic efficiency
  - Biomass is 60% oil
- Looked for lipid “trigger”
- Genetic manipulation
  - Mutagenesis and selection
  - Genetic engineering
New Research

- New NERL initiative
  - Funded by Chevron
  - Focus
    - Maximize oil content
    - Maximize growth rate
    - Control production costs
  - Compliments separate NERL program focusing on hydrogen generation from algae
Extraction of Oils

- **Chemical**
  - Benzene, hexane, petroleum ether

- **Enzymatic**
  - Enzymatic breakdown of cellular walls
  - Cellular water used as solvent
  - More expensive than chemical extraction

- **Mechanical**
  - press
Extraction of Oils

- Osmotic shock
  - Drop in osmotic pressure causes cells to rupture
- Supercritical fluid
  - Liquefied CO$_2$ extraction
- Sonochemistry
  - Ultrasonic assisted extractions
Fuel Types

- **Biomass**
  - Burn to generate electricity and heat

- **Methane**

- **“Straight vegetable oil” (SVO)**
  - Oil from algae can be mixed directly with petroleum diesel (up to 50% mixture)
  - Modified diesel engine can run on 100% algae oil
Fuel Types

- Ethanol
  - Can be used directly as a fuel or blended with gasoline
  - Starches converted to ethanol
    - $\text{C}_6\text{O}_6\text{H}_{12} \rightarrow 2 \text{C}_2\text{H}_5\text{OH} + \text{CO}_2$

- Transportation fuels
  - Oil of *Botryococcus braunii* chemically reduced to transportation fuels (octane, diesel, aviation grade kerosene)
Fuel Types

- Non-biological hydrogen production
  - Water gas-shift reaction
  - \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)
Fuel Types

- Biological production of hydrogen
  - First observed by Hans Gaffron in 1939
  - 1990’s Anastasios Melis discovers that sulfur deprivation switches photosynthesis to produce hydrogen
  - Most work done with *Chlamydomonas reinhardtii*
    - Genetically modified Stm6 strain
      - Produces 5 times more hydrogen
      - ~2% energy efficient
  - 2006 shortened chlorophyll stack, increased efficiency to ~ 10%
Fuel Types

Glycolysis | Tricarboxylic acid cycle

-600 | cytoplasm
-200 | chloroplast
0 | 
+200 | 
+600 | 
+1,000 mV |

Red

NAD(P)H
NAD(P)⁺

Q
PQ
Cyt b
Cyt f
PC

A
Fd
FNR

H₂ase

H₂
2H⁺
NAD⁺
NADPH

P₇₀₀
PS I

P₆₈₀
PS II

O₂ + 4e⁻ + 4H⁺
2H₂O

hv

hv
Fuel Types

- Biological production of hydrogen (cont)
  - Nitrogenases
    - Requires 2 molecules of ATP for each electron
    - Decreases overall quantum efficiency
  - Hydrogenases
    - \[2H^+ + 2e^- = H_2\]
    - Does not require ATP
    - Active enzyme – turnover rate \(10^6\) s\(^{-1}\)
    - Inhibited by oxygen
Fuel Types

- Biological production of hydrogen (cont)
  - Estimated production rates for *C. reinhardtii*
    - 5 mL / hour / L of culture
  - An estimated 25,000 km² of algae would be needed to produce enough hydrogen to replace gasoline in the U.S.
    - Area the size of Vermont
    - Less than 1/10 of the land area currently used to grow soy in the U.S.
Fuel Types

- **Biodiesel**
  - Transesterification of oil from algae
    - Formation of fatty acid methyl esters (FAME)
    - Reaction of oil with alcohol
      - Can use methanol, ethanol, propanol, butanol, and amyl alcohol
        - Methanol and ethanol frequently used due to low cost
    - Acid catalyzed or alkali catalyzed reaction
  - Glycerol separated by settling or centrifugation
Fuel Types

Overall Reaction

Triglycerides (Vegetable Oils)

Alcohol (Usually Methanol)

Acid or Base Catalyst

Alkyl esters (Biodiesel)

Glycerol

Triglyceride Reaction

Diglyceride Reaction

Monoglyceride Reaction
Fuel Types

Cellulosic Biomass

Gasification

SynGas (CO + H₂)

Pyrolysis or Liq

Fischer-Tropsch

Methanol

Water-Gas Shift

Alkanes

Methanol

Hydrogen

Bio-oils (Including tars, acids, char, alcohols, aldehydes, esters, ketones and aromatic)

Dehydrogenation

Zeolite Upgrading

Liquid Fuels

Liquid Fuels

Aqueous Sugar

Fermentation

Aromatic Hydrocarbons

Dehydration

Liquid Alkanes or Hydrogen

Aqueous-Phase Processing

Etherified gasoline

Lignin

Fermentation

Lignin Upgrading

Ethanol

Aromatic Hydrocarbons

Dehydration

Liquid Alkanes or Hydrogen

Aqueous-Phase Processing

Etherified gasoline
advantages

- High growth rate (some species can double mass overnight)
- High oil content (some species up to 50% oil)
- Can be harvested daily (species dependant)
- Can be used to recycle / sequester carbon dioxide
Advantages

- **Environmental**
  - Tie into local coal-fired power plants and sewage treatment plants

- **Oil**
  - Contains no sulfur
  - Non-toxic
  - Biodegradable
  - Less particulate matter than diesel
Advantages

- Estimates (from Global Petroleum Club)

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<th>Crop</th>
<th>Yield</th>
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<tr>
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<tr>
<td>Soya</td>
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<tr>
<td>Canola</td>
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<tr>
<td>Oil Palm</td>
<td>6,000</td>
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<tr>
<td>Algae</td>
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Disadvantages

- Difficult to go from lab-scale to full production
- Open ponds susceptible to local strains
  - Local strains actually grow better than those inoculated
- Expensive capital investment / upkeep costs
- Biodiesel contains higher NO\textsubscript{x} levels
Co Products

- Additional uses to make algae production more economically viable:
  - Plastics
  - Pigments
  - Feedstock
  - Pharmaceutical / nutritional
  - Pollution control
Current Initiatives

- **Enhanced Biofuels & Technologies** ([www.ebtplc.com](http://www.ebtplc.com)) develops multiple vegetable oil Biofuel technologies. The EBT algae process combines a bioreactor with an open pond, both using waste CO2 from coal-fired power plant flue gases as a fertilizer for the algae. The biodiesel and ethanol produced can be sold, or used as an alternative fuel. Emissions are reduced up to 82%. EBT’s headquarters are in London, UK and the company has a biofuel R&D centre in India.

- **GreenFuel Technologies** ([www.greenfuelonline.com](http://www.greenfuelonline.com)) - *Emissions-to-Biofuels™* process harnesses photosynthesis to grow algae, capture CO2 and produce high-energy biomass. Retrofitting fossil-fired power plants and other anthropogenic sources of carbon dioxide, the algae can be economically converted to solid fuel, methane, or liquid transportation fuels such as biodiesel and ethanol.

- **GreenShift** ([www.greenshift.com/news.php?id=97](http://www.greenshift.com/news.php?id=97)) has a license agreement with Ohio University for its patented bioreactor process based on a newly discovered iron-loving cyanobacterium (blue-green algae), through their subsidiary Veridium ([www.veridium.com](http://www.veridium.com)), for the purpose of air pollution control of exhaust gas streams from electrical utility fossil-fuelled power generation facilities. Once the algae grow to maturity, they fall to the bottom of the bioreactor and are harvested for fuel or fertilizer.

Current Initiatives

- **Solazyme** ([www.solazyme.com](http://www.solazyme.com)) is devoted to harnessing the energy-harvesting machinery of various species of algae to produce valuable products. The company utilizes proprietary genetic engineering methods to develop and optimize commercially relevant biochemical pathways for production of hydrocarbons (for energy and specialty chemicals) & bioactive compounds.

- **LiveFuels** ([www.livefuels.com](http://www.livefuels.com)) - A national alliance of labs and scientists dedicated to transforming algae into biocrude by the year 2010. Working on breeding various strains of algae, driving down the costs of harvesting algae and extracting fats and oils from the algae.

- **Valcent Products** ([www.valcent.net/news_detail.sstg?id=36](http://www.valcent.net/news_detail.sstg?id=36)) has developed a high density vertical bio-reactor for the mass production of oil bearing algae while removing large quantities of CO2 from the atmosphere. This new bio-reactor is tailored to grow a species of algae that yields a large volume of high grade vegetable oil, which is very suitable for blending with diesel to create a bio-diesel fuel.

Current Initiatives

- **Aquaflow Bionomics Corporation** (*aquaflowgroupcom.axiion.com*), New Zealand-based, has set itself the objective to be the first company in the world to economically produce biofuel from wild algae harvested from open-air environments and to market it.

- **Infinifuel Biodiesel** (*www.infinifuel.com*) - Wabuska Nevada is home to a unique biodiesel project under development and is being touted as the world’s first geothermal-powered and heated biodiesel plant. The existing geothermal power plant features two production wells and seven power production units creating more than 5 MW of electricity, according to Infinifuel. The power plant will provide 2 MW of electricity and 104°C (220°F) steam to the biodiesel facility, which is nearing completion. The company has over 300 acres to grow oil-seed and develop algae ponds on site.

Current Initiatives

- **Solix Biofuels** ([www.solixbiofuels.com](http://www.solixbiofuels.com)) is a developer of massively scalable photo-bioreactors for the production of biodiesel and other valuable bio-commodities from algae oil. Solix’ closed photo-bioreactors allow fossil-fuel power plant exhaust to be captured through the growing system. The algae growth rates increase in the presence of the carbon dioxide that would otherwise be emitted into the atmosphere.

- **Algoil** ([www.algoil.com](http://www.algoil.com)) is a pioneer project focusing on the production of biodiesel/biomass from micro-algae. The target is to use the rest of the extracted biomass to make food, biofuel, hydrogen, paper, or simply burning it like charcoal.

Current Initiatives

- PetroAlgae (www.petroalgae.com) is commercializing environmentally-friendly algae developed by a research team at Arizona State University that generates over two hundred times more oil per acre than crops like soybeans. Using a cost-effective, modular cultivation process that can be massively scaled, PetroAlgae will produce renewable feedstock oils for use in applications such as transportation fuels, heating oil, and plastics.

- Aurora BioFuels (www.aurorabiofuels.com) is a California-based renewable energy company exploring new sources of feedstock for the production of biofuels. In particular, Aurora focuses on utilizing microalgae to generate bio-oil, which can be converted into biodiesel.

Conclusions

- Renewable alternative to petroleum based fuels
- Not the sole solution to renewable energy
  - only part of the solution
- Needs more research to make the process economically viable
References

http://en.wikipedia.org/wiki/algaculture
http://en.wikipedia.org/wiki/Biofuel_from_algae


Berg-Nilsen, Jan, Production of Micro Algae-Based Products, Norden (Nordic Innovation Centre) Report, August 2006

References


References


*A Look Back at the U.S. Department of Energy’s Aquatic Species Program: Biodiesel from Algae*, Close-Out Report, NREL/TP-580-24190
Thank You

Questions?