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BS, Massachusetts Institute of Technology, June 2021
(Chemical-biological Engineering, Computer Science & Molecular Biology)

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Diversity, Equity, Inclusion, and Respect

Equity**
- "Seeks to ensure treatment, equality of opportunity, and fairness in access to information and resources for all. We believe this is only possible in an environment built on respect and dignity. Equity requires the identification and elimination of barriers that have prevented the full participation of some groups."

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Inclusion**
- "Builds a culture of belonging by actively inviting the contribution and participation of all people. Every person’s voice adds value, and ACS strives to create balance in the face of power differences. In addition, every person can and should be called upon to represent the entire community."

Respect
- "Ensures that each person is treated with professionalism, integrity, and ethics underpinning all interpersonal interactions."

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**Diversity, Equity, Inclusion, and Respect**
- "Inspired from individuals from the Mentorship Center for Women Scientist"

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Empowering people to reimagine chemistry and engineering for a sustainable future.

**Vision**
A sustainable future facilitated by the transforming power of chemistry and engineering.

**Mission**
To catalyze the implementation of innovative approaches to chemistry and engineering that enable sustainable development across the globe.

**Strategic Areas**

<table>
<thead>
<tr>
<th>Science</th>
<th>Education</th>
<th>Industry</th>
<th>Equity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advance research, scholarship and innovation in green and sustainable chemistry and engineering</td>
<td>Enable the implementation of green chemistry and engineering across the education sector</td>
<td>Accelerate the industrial adoption of green and sustainable chemistry and engineering</td>
<td>Facilitate equity in the adoption of green chemistry, engineering, and sustainability practices worldwide</td>
</tr>
</tbody>
</table>

ACS Campaign for a Sustainable Future

SUMMITS: MOBILIZE CHEMISTS TO CONTRIBUTE TO SDG’S
GREEN AND SUSTAINABLE CHEMISTRY PLATFORM
SUSTAINABLE CHEMISTRY GRANTS PROGRAM

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CENTER FOR GREEN CHEMISTRY & GREEN ENGINEERING AT YALE

Integrated Algae Biorefinery

Julie Beth Zimmerman, PhD
Professor | School of Engineering and Applied Sciences
Professor and Senior Associate Dean | School of the Environment
Editor in Chief | Environmental Science & Technology

PROBLEM SOLUTION
Provide clean water without using and generating toxic chemicals

Generate energy without altering the atmosphere

Produce goods and services without depleting finite resources and generating waste

Grow food without polluting our water with fertilizers and pesticides

Provide healthcare without harming public health

Be efficient without continuing to increase absolute emissions

That is, we want our solutions to meet societal needs in ways that are conducive to life… today and in the future.
This requires changing the **inherent nature** of our materials and energy sources.

This will lead to solutions that are:

- renewable not depleting,
- healthful not toxic, and
- restorative not degrading.

So how do we get the problem statement right?
So how do we get the problem statement right?

The same way we get the solutions right.

by coupling reductionism with systems thinking.

The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a "constructionist" one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the ele-

18
by coupling reductionism with systems thinking.

by coupling innovation with sustainability.

by coupling discovery with development.

by coupling implementation with scale.
Urgent Need

One Hundred Tenth Congress of the United States of America
AT THE FIRST SESSION

Begun and held at the City of Washington on Thursday, the fourth day of January, two thousand and seven

HOW GREEN ARE BIOFUELS?

FUEL SOURCES

Diesel
Other Distillates
Jet Fuel
Other Products
Heavy Fuel Oil
Liquified Petroleum Gases
Gasoline

*U.S. Energy Information Administration: www.eia.gov
Context: Integrated Biorefinery

Processing:
- Harvesting/dewatering possibilities include (78):
  - Flotation and sedimentation (79,81)
  - Electrocoagulation (82)
  - Fiber press and centrifugation (87)
  - Tangential flow filtration (84)
  - Suspended air flotation (85)

Algal Biomass:
- Composition will vary by:
  - Species
    - Fresh vs. Salwater (74, 81)
  - CMOs vs. wild-type (87)
  - Auto- vs. Heterotrophic (88-89)

Growth conditions:
- FBR vs. Ranneray (71, 82)
- Nutrient loading (93, 95)
- Temperature (86-88)

Non-polar Lipids: Proteinaceous Wet
- FAME/FAEE/EEC (53, 99, 204)
- Glycerol products (96, 94-98)
- PLA/PLA (100)
- Lipids (100)
- Polylactic (101)
- Polymers (102)
- Polynucleotides (21)
- Fatty alcohols (46)
- Fatty acids (46)
- Nutraceuticals (44)
- Animal feed (33)
- Steroids (29)
- Biofuels (66, 431)
- Bioplastics (63)
- Commodity chemicals (69-70)
- Food additives (35, 39)

Polar Lipids: Predominantly phospholipids, sphingolipids, and glycolipids

Pigments and Stellars:
- Includes high value antioxidants such as astaxanthin and 5-carnitine

Starch and Other Glucans

Alginate and Complex Polyelectrolytes

Amino Acids

Secondary Metabolites and Inorganics

Context: Cellular Composition

Context: Supercritical Fluid

![Supercritical Fluid Diagram]

Context: Transesterification

Fatty Acid Methyl Esters (FAME) - Biodiesel

- Triglyceride (TG) + Methanol + Catalyst → Diglyceride (DG) → Monoglyceride (MG) → Glycerol
- CO₂

![Transesterification Diagram]
Why are some algal biorefineries carbon negative and others not?


What are the highest impacts of the current biorefinery system?

Assessment informs design…

Develop and optimize improved extraction/conversion process for biomass to biodiesel, other fuels and chemicals.

Is it efficacious?


Can it be as efficacious as current technology?

Is it beneficial over current technology?


<table>
<thead>
<tr>
<th></th>
<th>Conventional Extraction</th>
<th>Extracted with SFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C</td>
<td>70.44 ± 0.08</td>
<td>72.92 ± 0.41</td>
</tr>
<tr>
<td>% H</td>
<td>11.09 ± 0.10</td>
<td>11.77 ± 0.11</td>
</tr>
<tr>
<td>% N</td>
<td>0.58 ± 0.01</td>
<td>0.42 ± 0.04</td>
</tr>
<tr>
<td>Ratio H/C</td>
<td>0.157</td>
<td>0.161</td>
</tr>
<tr>
<td>Ratio N/C</td>
<td>0.0082</td>
<td>0.0058</td>
</tr>
</tbody>
</table>
Is it beneficial over current technology?

![Chart showing FAME extracted (mg/g algae) vs. Volume water added (ml)]


Can we exploit CO2 properties to be more selective?

![Bar chart showing the concentration of fatty acids in Chlorococcus sp. with varying supercritical CO2 densities]

Can we do extraction and conversion in one pot?

Starting material: Triolein, 10mg = 34 µmol ester
Reaction time: 2h
Catalyst: Nafion, 10 beads = 18.5 – 470 µEq H^+ 

Optimal Point: 80°C, 9.65 MPa, 3.6% Methanol loading (vol/vol)

Is it the CO2?


Why is it efficacious?

Measured at 80°C at 3.6% methanol loading equivalent

What are the optimum conditions?

95°C → > 98% yield

Surface model optimization at 3.6% methanol loading equivalent


How do we improve further?

Path Forward

Value Products

- Triacylglycerides (TAG)
- Bioactive compounds
  - Carotenoids
    - Astaxanthin
  - ω-3 fatty acids
    - Eicosapentaenoic acid (EPA)
    - Docosahexaenoic acid (DHA)
- Towards biorefinery realization
  - Close economic gaps
Super Complex System

- Pressure
- Temperature
- Modifier content
- Flow rate
- Analyte solubility
- Drying, milling, grinding
- Bed porosity
- Bed geometry
- Apparent density (mass loading)
- Particle size and distribution
- Particle geometry
- Real density of solid particles
- Initial analyte content in substrate
Tuning Potential

**CO₂ Isotherm**

Tuning “Green”

**CO₂ Isotherm**
Investigating inherency

Extraction Curves

Sovova, H.; Mathematical model for supercritical fluid extraction of natural products and extraction curve
Experimental Setup

- Particle size
  - <0.595mm, >0.354mm
- 25 mL vessel
- 200 mg
  - Analytical standards
    - *Scenedesmus dimorphus*
    - *Haematococcus pluvialis*
- 3-5 mg CO₂ per minute

Multi-Component

![Graph showing cumulative TAG extract (m g) vs. CO₂ delivered (m g) for various TAG species with 750 mg/m l CO₂.](image)
Scenedesmus dimorphus
Enrichment

![Graph showing enrichment of TAG and CO2 density.](http://www.nutrex-hawaii.com/)
Red Antioxidant

- Carotenoids
  - Astaxanthin

Capelli, B., et. al., Synthetic astaxanthin is significantly inferior to algal-based astaxanthin as an antioxidant and may not be suitable as a human nutraceutical supplement. Nutrafoods, 2014. 12(4)

Haematococcus pluvialis

![Graph showing the relationship between CO₂ delivered and triacylglycerides, and astaxanthin content.](Graph Image)
Dynamic Control

• Static control
  – Single density & polarity
  – Single operational parameters
    • Temperature
    • Pressure
    • Entrainer

• Dynamic control
  – Multiple densities & polarities

Astaxanthin
Kwan TA, Kwan SE, Peccia J, Zimmerman JB. Selectively biorefining astaxanthin and triacylglycerol co-products from microalgae with supercritical carbon dioxide extraction. Bioresource technology. 2018 Dec 1;269:81-8.

Back of the Envelope

- Biodiesel → $7/kg
- Astaxanthin → $7000/kg
- CO$_2$ credits → ?/kg
More value to find from an integrated biorefinery

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