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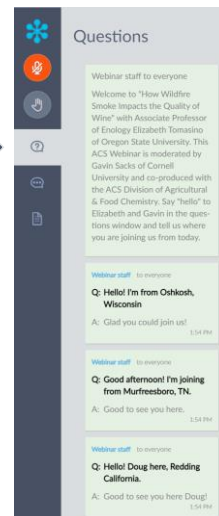
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**"Why am I muted?"**

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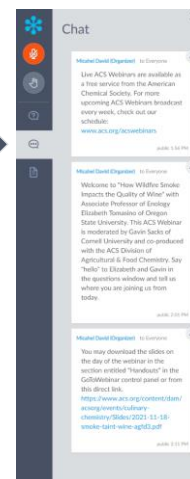


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**Chat**

Announcements and hyperlinks from our team



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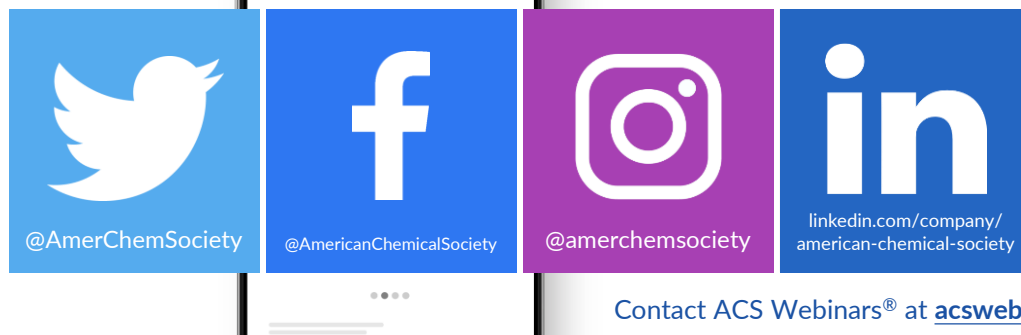


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## A Career Planning Tool For Chemical Scientists



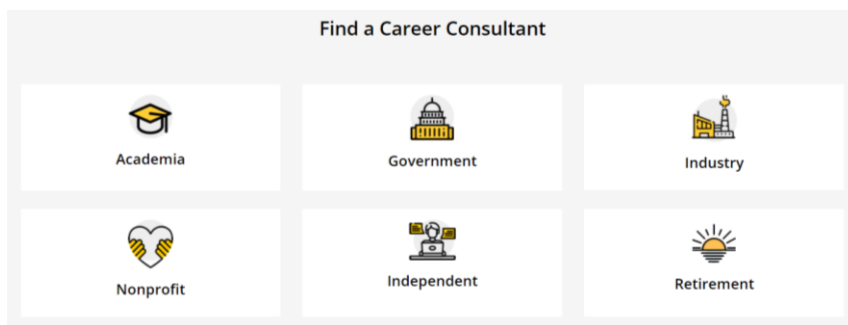
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<p><b>Virtual Classrooms</b> Brought to you by ACS Career Pathways™, free online modules and virtual experts to help you reach your career goals.</p>	<p><b>ACS Webinars</b> Hundreds of webinars presented by subject matter experts in the chemical and allied fields.</p>	<p><b>Career Events</b> Free webinars and networking opportunities for mid-career chemistry professionals.</p>
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<p><b>3 AUG</b></p> <p><b>Careers in Government</b></p> <p>○ August 3, 2023</p>	<p><b>7 SEP</b></p> <p><b>The Basics of Building Resilience</b></p> <p>○ September 7, 2023</p>
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### ACS Scholar Adunoluwa Obisesan

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

*"The ACS Scholars Program provided me with monetary support as well as a valuable network of peers and mentors who have transformed my life and will help me in my future endeavors. The program enabled me to achieve more than I could have ever dreamed. Thank you so much!"*

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Advancing ACS' Core Value of Diversity, Equity, Inclusion and Respect



## Resources

<b>Inclusivity Style Guide</b> Designed to help staff and members use language and images that respect diversity in all its forms. →	<b>ACS Webinars on Diversity</b> Covering diversity and inclusion at the workplace →
<b>ACS Publications DEIR Hub</b> See what ACS Publications is doing for fostering inclusivity in scholarly publishing →	<b>ACS Volunteer and ACS Meetings Code of Conduct</b> Fostering a positive and welcoming environment for attendees, volunteers and staff. →
<b>C&amp;EN Trailblazers</b> C&EN highlights scientists from different backgrounds who are making an impact in chemistry. →	<b>NEW! Download DEIR Educational Resources</b> Download this educational guide for additional recommendations on videos, articles, books, podcasts, and more on diversity, inclusion, and related topics. →
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## Diversity, Equity, Inclusion, and Respect

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### Diversity\*\*

The representation of varied identities and differences (race, ethnicity, gender, disability, sexual orientation, gender identity, national origin, tribe, caste, socioeconomic status, thinking and communication styles, etc.), collectively and as individuals. ACS seeks to proactively engage, understand, and draw on a variety of perspectives.

### 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, no one person can or should be called upon to represent an entire community.

### Respect

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

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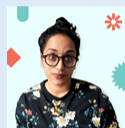
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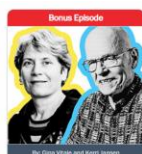
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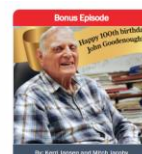
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Carolyn Bertozzi and K. Barry Sharpless chat about sharing the 2022 Nobel Prize in Chemistry  
December 6, 2022



**Bonus Episode**  
Bioorthogonal, click chemistry clinch the Nobel Prize  
October 5, 2022



**Episode #46**  
Lithium mining's water use sparks bitter conflicts and novel chemistry  
September 13, 2022



**Bonus Episode**  
Happy 100th birthday, John Goodenough!  
For John Goodenough's 100th birthday, Stereo Chemistry revisits a fan-favorite interview with the renowned scientist  
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<p><b>Quick Guide: Inclusion Moments</b></p> <p>Learn more about what Inclusion Moments are and see ideas to host them during your meetings.</p> <p>→</p>	<p><b>Quick Guide: How to host inclusive in-person events</b></p> <p>Recommendations and best practices to ensure that your events can accommodate everyone.</p> <p>→</p>



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



ACS

Chemistry for Life®

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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

Science	Education	Industry	Equity
Advance research, scholarship and innovation in green and sustainable chemistry and engineering	Enable the implementation of green chemistry and engineering across the education sector	Accelerate the industrial adoption of green and sustainable chemistry and engineering	Facilitate equity in the adoption of green chemistry, engineering, and sustainability practices worldwide

American Chemical Society

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REBROADCAST

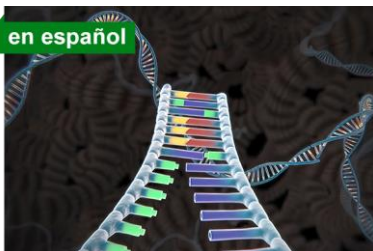


Thursday, April 20, 2023 | 2-3pm ET

### Cannabinoids: Stumbling Through Challenging Separations (Rebroadcast)

Co-produced with ACS Office of Career and Professional Education

en español



Wednesday, April 26, 2023 | 2-3pm ET

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NEXT WEEK!



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**AMAZING ALGAE**

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## **Towards an Integrated Algae Biorefinery:** Extraction, Fractionation, Purification, and Transformations in Green Solvents



**JULIE ZIMMERMAN, PhD**

Senior Associate Dean of Academic Affairs,  
Professor of Green Engineering, Assistant Director  
for Research at Center for Green Chemistry and  
Green Engineering, Yale University



**ADELINA VOUTCHKOVA-  
KOSTAL, PhD**

Director, Office of Sustainability,  
American Chemical Society



**DAVID A. LAVISKA, PhD**

Portfolio Manager, Green Chemistry &  
Sustainability in Education, Green  
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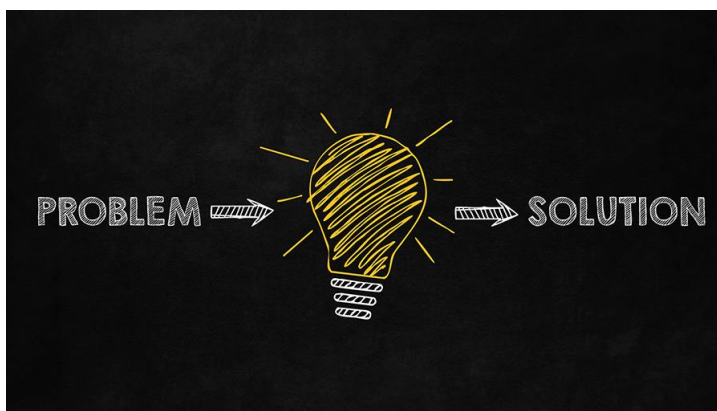
# Integrated Algae Biorefinery

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*

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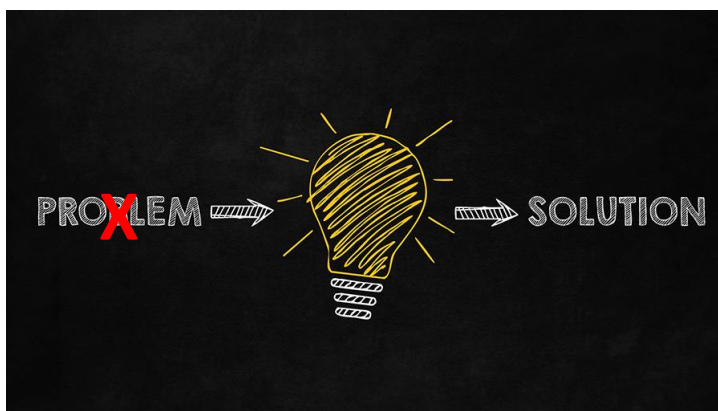


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CENTER FOR GREEN CHEMISTRY & GREEN ENGINEERING AT YALE



CENTER FOR GREEN CHEMISTRY & GREEN ENGINEERING AT YALE





- |                            |   |
|----------------------------|---|
| 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 the polluting our water with fertilizers and pesticides |
| Provide healthcare         | without harming public health                                   |
| Be efficient               | without continuing to increase absolute emissions               |



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That is, we want our solutions to meet societal needs in ways that are conducive to life... today and in the future.



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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.**



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PROBLEM

So how do we  
get the problem  
statement right?



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**PROBLEM**

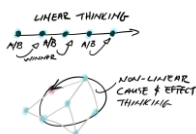
So how do we get the problem statement right?

The same way we get the solutions right.

**SOLUTION**



by coupling reductionism with systems thinking.



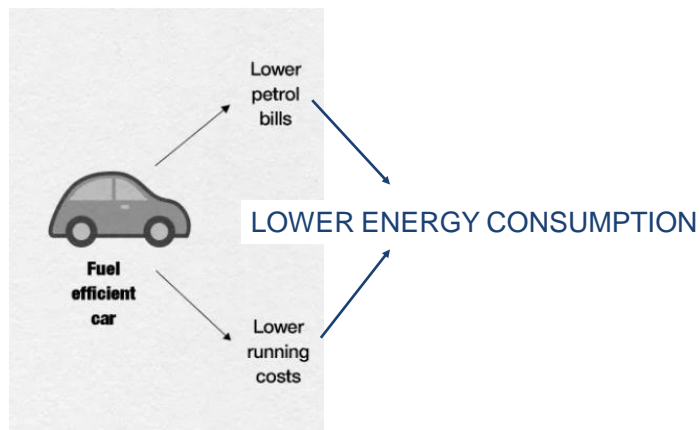
4 August 1972, Volume 177, Number 4047

**SCIENCE**

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-

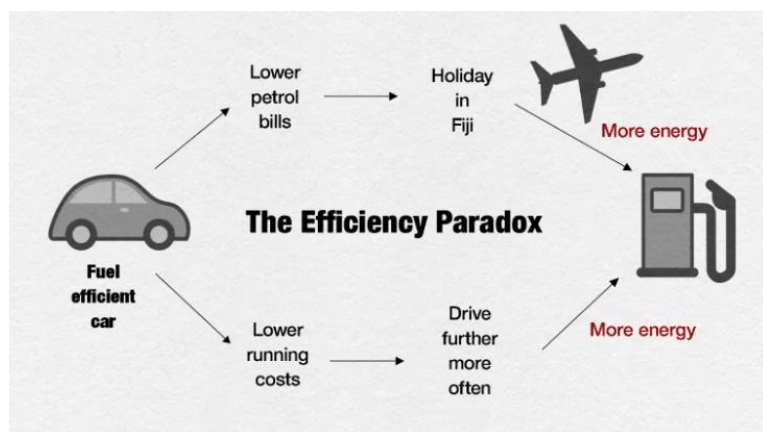
...try the  
...ity in a hierarchy,  
according to the idea. The elementary  
... of science X obey the laws of  
science Y.  
... in most cases. Solid  
... ions, plasma physics, and perhaps  
also biology are extensive. High energy





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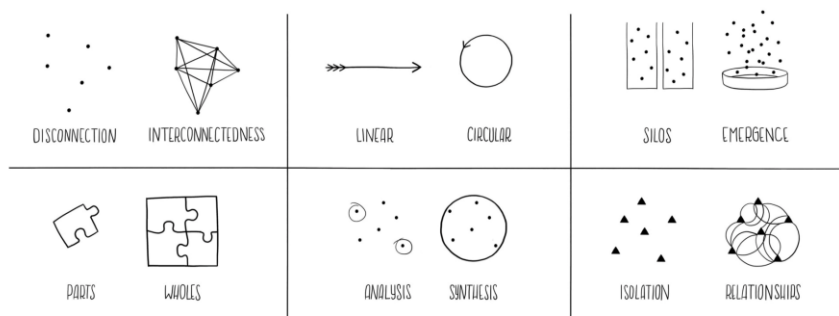
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## TOOLS OF A SYSTEM THINKER



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by coupling  
reductionism with  
systems thinking.

by coupling  
innovation with  
sustainability.



by coupling  
discovery with  
development.

by coupling  
implementation  
with scale.

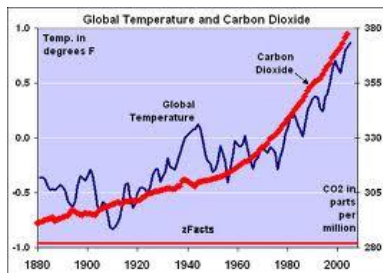


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# Urgent Need



One Hundred Tenth Congress  
of the  
United States of America

AT THE FIRST SESSION

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



### HOW GREEN ARE BIOFUELS?

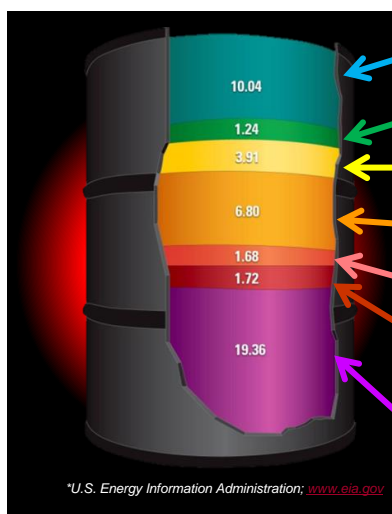
Biofuels are getting a bad rap as stories of rising prices and shortages fill the news. But the environmental, energy and land use impacts of the crops used to make the fuels vary dramatically. Current fuel sources – corn, soybeans and canola – are more harmful than alternatives that are under development.

CROP	USED TO PRODUCE	GREENHOUSE GAS EMISSIONS <sup>a</sup> (CO <sub>2</sub> e) grams emitted per gallon of fuel produced	USE OF RESOURCES DURING GROWING, HARVESTING AND BURNING OF FUEL				PERCENT OF EXISTING U.S. CROP LAND NEEDED TO PRODUCE ENOUGH FUEL TO MEET 2010 DEMAND	PROS AND CONS
			WATER	FERTILIZER	PESTICIDE	ENERGY		
Corn	Ethanol	81-85	high	high	high	high	157%-262%	Technology ready and relatively cheap; reduces food supply
Sugar cane	Ethanol	4-12	high	high	med	med	46-57	Technology ready, limited as to where will grow
Switch grass	Ethanol	24	med-low	low	low	low	69-108	Won't compete with food crops; technology not ready
Wood residue	Ethanol, biodiesel	N/A	med	low	low	low	150-250	Uses timber waste and other debris; technology not fully ready
Soybeans	Biodiesel	49	high	low-med	med	med-low	180-240	Technology ready; reduces food supply
Rapeseed, canola	Biodiesel	37	high	med	med	med-low	30	Technology ready; reduces food supply
Algae	Biodiesel	-183	med	low	low	high	1-2	Potential for large production levels; technology not ready

<sup>a</sup> Emissions produced during the growing, harvesting, selling and burning of fuel. Gasoline is 94, diesel is 83. Source: Markita Green, University of Washington; Elizabeth Gray, The Nature Conservancy; Patrick Townsend, University of Washington; as published in Conservation Biology 16(4):712-714



# Gallons in a Barrel

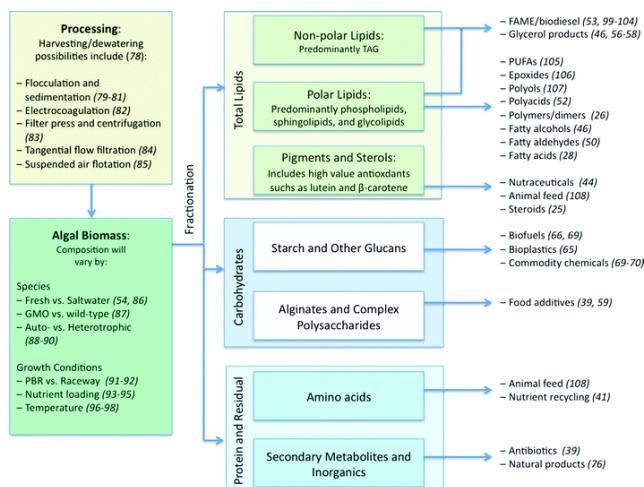


- Diesel
- Other Distillates
- Jet Fuel
- Other Products
- Heavy Fuel Oil
- Liquified Petroleum Gases
- Gasoline

\*U.S. Energy Information Administration; [www.eia.gov](http://www.eia.gov)



## Context: Integrated Biorefinery

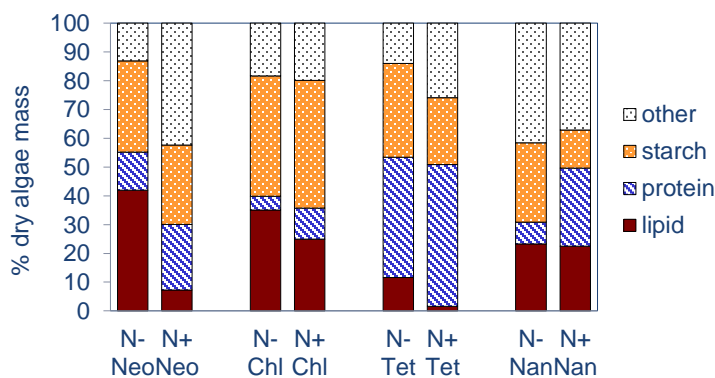


Foley, PM; Beach, ES; Zimmerman, JB. *Green Chem.* 2011, **13**, 1399-1405

43

43

## Context: Cellular Composition

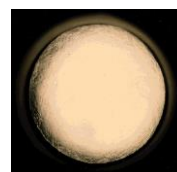
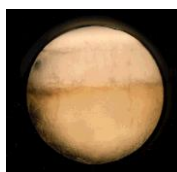
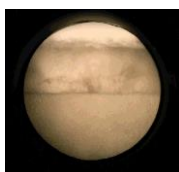
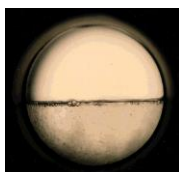
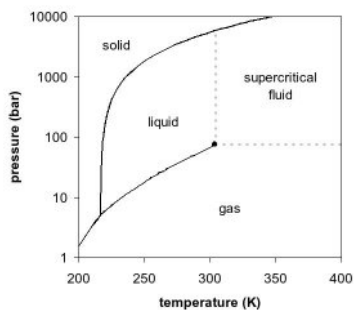


Soh, L., Eckelman, M.J., Haznedaroglu, B.Z., Kelly, C.O., Peccia, P., Zimmerman, J.B. 2014.

44

44

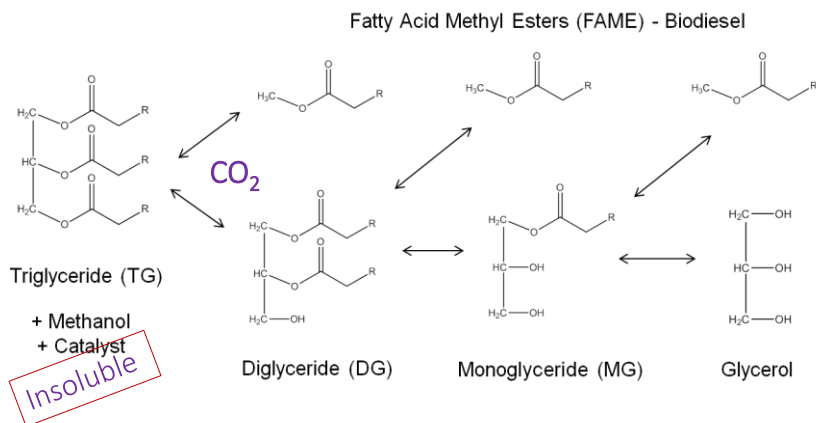
## Context: Supercritical Fluid



45

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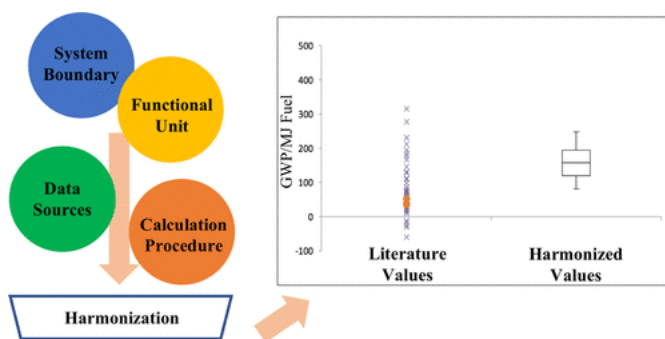
## Context: Transesterification



46

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## Why are some algal biorefineries carbon negative and others not?

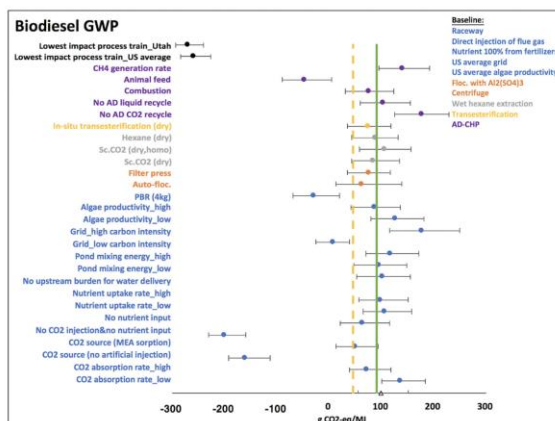


Tu Q, Eckelman M, Zimmerman J. Meta-analysis and harmonization of life cycle assessment studies for algae biofuels. *Environmental science & technology*. 2017 Sep 5;51(17):9419-32.

47

47

## Why are some algal biorefineries carbon negative and others not?



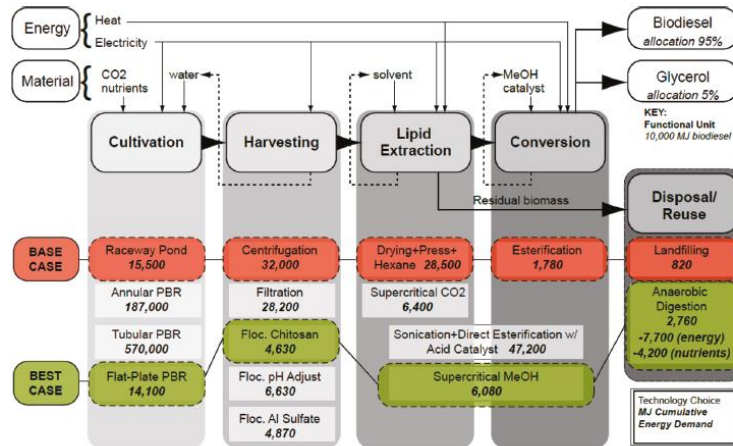
Tu Q, Eckelman M, Zimmerman JB. Harmonized algal biofuel life cycle assessment studies enable direct process train comparison. *Applied energy*. 2018 Aug 15;224:494-509.

48

48



## What are the highest impacts of the current biorefinery system?



Brentner, Eckelman, Zimmerman, "Life cycle assessment of algal biodiesel: a model to guide process design for industrial production", ES&T, 2011, 45 (16), 7060-7067.

49

49

## Assessment informs design...

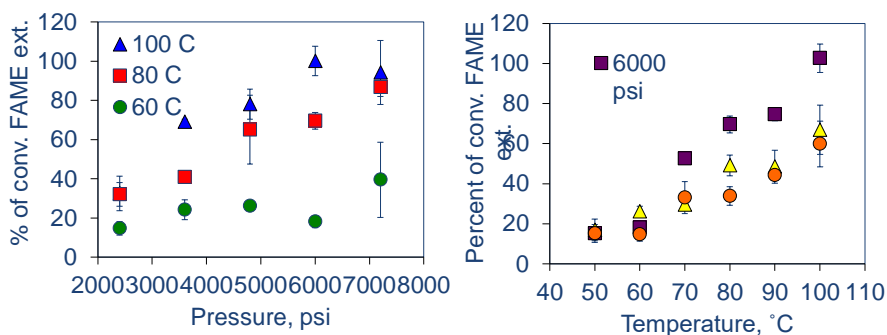
Develop and optimize improved extraction/conversion process for biomass to biodiesel, other fuels and chemicals.



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## Is it efficacious?

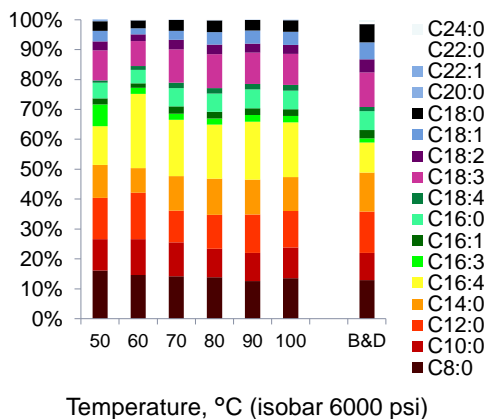


Soh, L.; Zimmerman, J. B., Biodiesel Production Potential of Algal Lipids Extracted with Supercritical Carbon Dioxide. *Green Chemistry* 2011, 13 (6), 1422-1429.

51

51

## Can it be as efficacious as current technology?

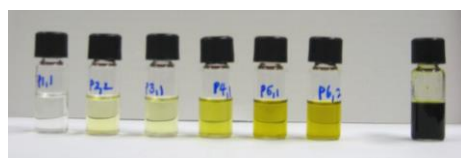
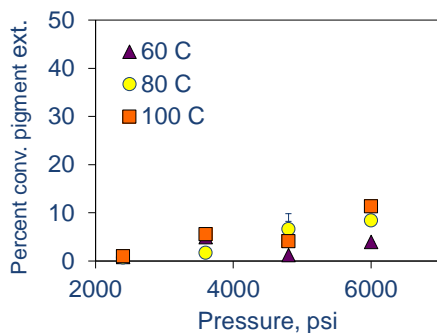


Soh, L.; Zimmerman, J. B., Biodiesel Production Potential of Algal Lipids Extracted with Supercritical Carbon Dioxide. *Green Chemistry* 2011, 13 (6), 1422-1429.

52

52

## Is it beneficial over current technology?

CO<sub>2</sub> extraction

organic solvent extraction



Soh, L.; Zimmerman, J. B., Biodiesel Production Potential of Algal Lipids Extracted with Supercritical Carbon Dioxide. *Green Chemistry* 2011, 13 (6), 1422-1429.

53

53

## Is it beneficial over current technology?

	Conventional Extraction	Extracted with SFE
% C	70.44 ± 0.08	72.92 ± 0.41
% H	11.09 ± 0.10	11.77 ± 0.11
% N	0.58 ± 0.01	0.42 ± 0.04
Ratio H/C	0.157	0.161
Ratio N/C	0.0082	0.0058

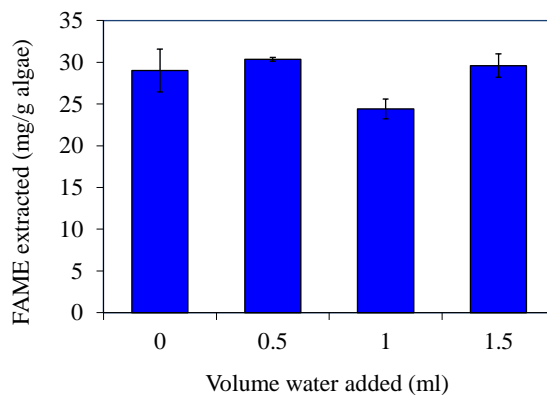


Soh, L.; Zimmerman, J. B., Biodiesel Production Potential of Algal Lipids Extracted with Supercritical Carbon Dioxide. *Green Chemistry* 2011, 13 (6), 1422-1429.

54

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## Is it beneficial over current technology?

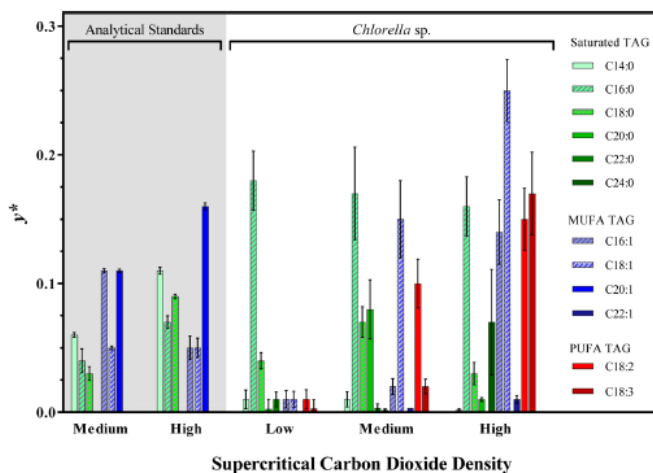


Soh, L.; Zimmerman, J. B., Biodiesel Production Potential of Algal Lipids Extracted with Supercritical Carbon Dioxide. *Green Chemistry* 2011, 13 (6), 1422-1429.

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## Can we exploit CO<sub>2</sub> properties to be more selective?

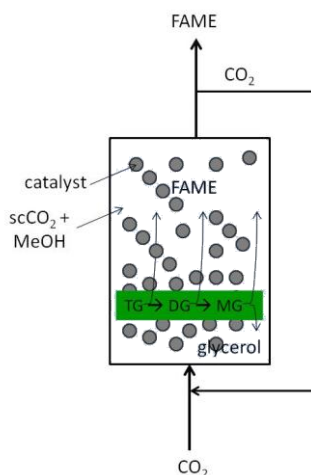


Kwan, T.A., Tu, Q. and Zimmerman, J.B., 2016. *ACS Sustainable Chemistry & Engineering*, 4(11), pp.6222-6230.

56

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## Can we do extraction and conversion in one pot?



57

57

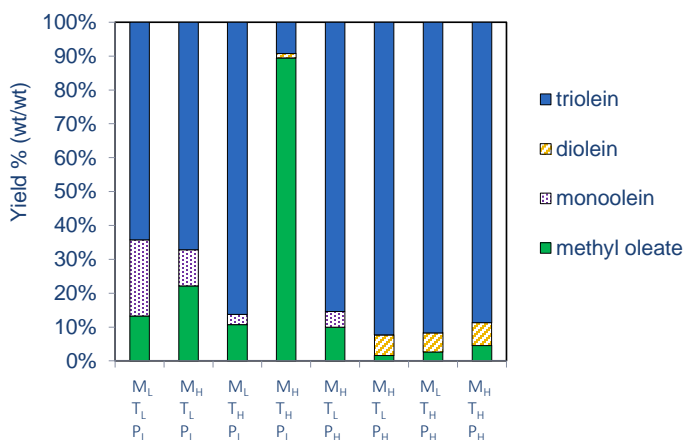
## Can it be as efficacious as current technology?

Starting material: Triolein,  
10mg = 34  $\mu$ mol ester

Reaction time: 2h

Catalyst: Nafion, 10 beads =  
18.5 – 470  $\mu$ eq H<sup>+</sup>

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

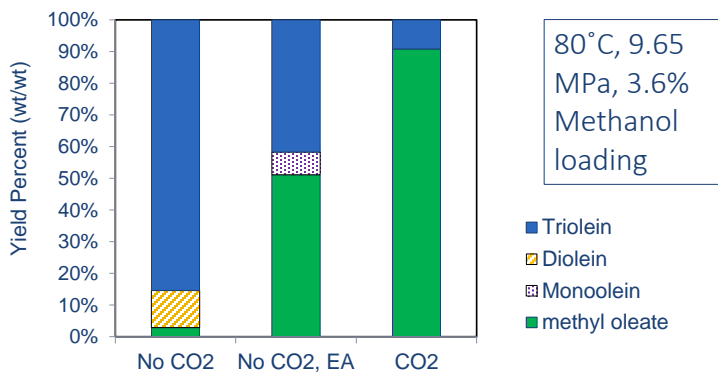


Soh, L., Curry, J., Beckman, E.J. and Zimmerman, J.B., 2013. Effect of system conditions for biodiesel production via transesterification using carbon dioxide–methanol mixtures in the presence of a heterogeneous catalyst. *ACS Sustainable Chemistry & Engineering*, 2(3), pp.387-395.

58

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## Is it the CO<sub>2</sub>?

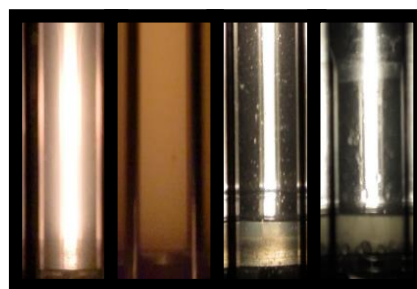
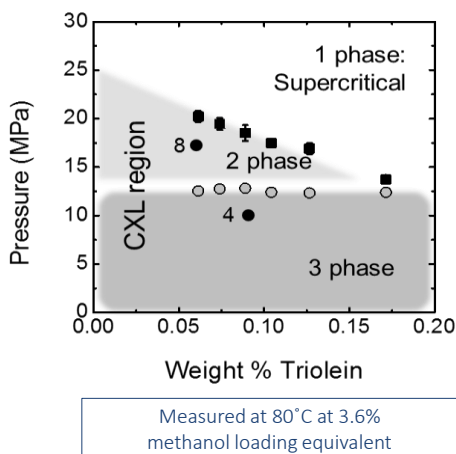


Soh, L., Curry, J., Beckman, E.J. and Zimmerman, J.B., 2013. Effect of system conditions for biodiesel production via transesterification using carbon dioxide–methanol mixtures in the presence of a heterogeneous catalyst. *ACS Sustainable Chemistry & Engineering*, 2(3), pp.387-395.

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## Why is it efficacious?



Differential solubilities across phases

Increased interaction of substrate and methanol



Soh, L., Curry, J., Beckman, E.J. and Zimmerman, J.B., 2013. Effect of system conditions for biodiesel production via transesterification using carbon dioxide–methanol mixtures in the presence of a heterogeneous catalyst. *ACS Sustainable Chemistry & Engineering*, 2(3), pp.387-395.

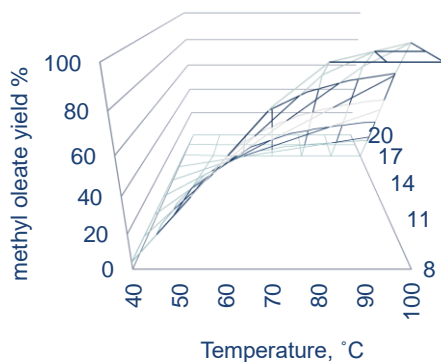
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## What are the optimum conditions?

95°C → > 98% yield



Surface model optimization at 3.6% methanol loading equivalent

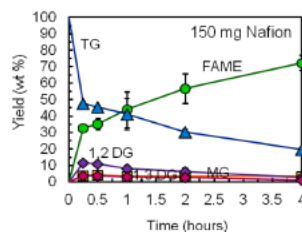
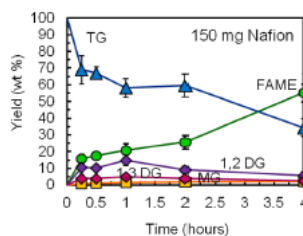


Soh, L., Curry, J., Beckman, E.J. and Zimmerman, J.B., 2013. Effect of system conditions for biodiesel production via transesterification using carbon dioxide–methanol mixtures in the presence of a heterogeneous catalyst. *ACS Sustainable Chemistry & Engineering*, 2(3), pp.387-395.

61

61

## How do we improve further?



3-4 mm  
mm

Nafion



0.25-0.5  
mm

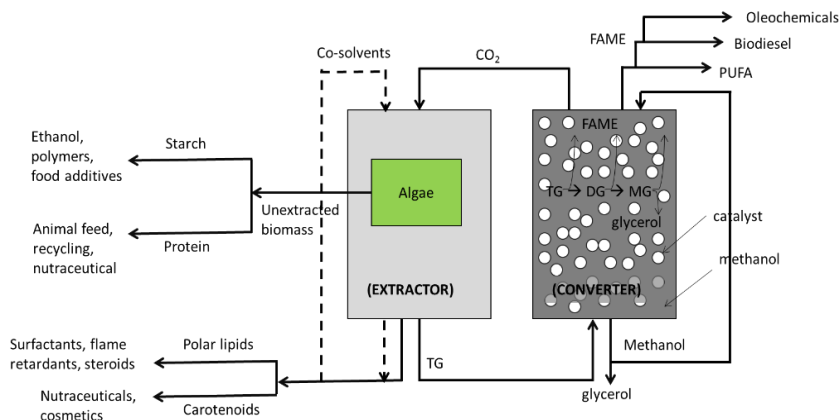


Soh, L., Chen, C.C., Kwan, T.A. and Zimmerman, J.B., 2015. Role of CO<sub>2</sub> in Mass Transfer, Reaction Kinetics, and Interphase Partitioning for the Transesterification of Triolein in an Expanded Methanol System with Heterogeneous Acid Catalyst. *ACS Sustainable Chemistry & Engineering*, 3(11), pp.2669-2677.

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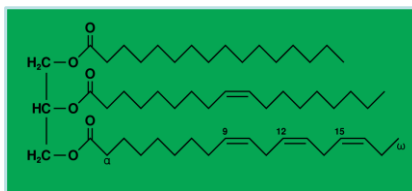
## Path Forward



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## Value Products

- Triacylglycerides (TAG)
  - Bioactive compounds
    - Carotenoids
      - Astaxanthin
    - $\omega$ -3 fatty acids
      - Eicosapentaenoic acid (EPA)
      - Docosahexaenoic acid (DHA)
- Towards biorefinery realization
  - Close economic gaps



64

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## 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



65

65

## Super Complex System

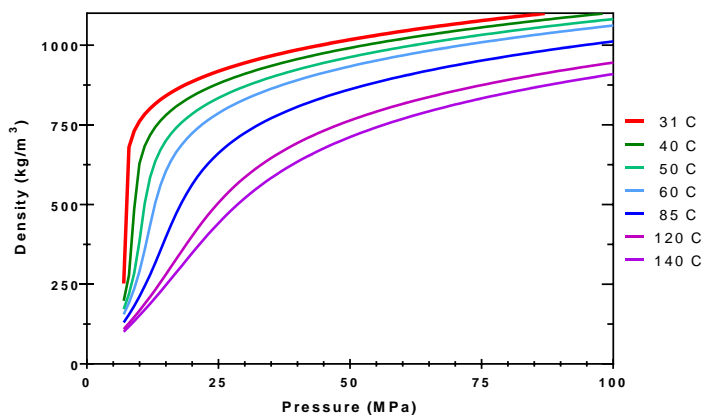
- Pressure
- Temperature
- Modifier content
- Flow rate
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- Bed porosity
- Bed geometry
- Apparent density (mass loading)
- Particle size and distribution
- Particle geometry
- Real density of solid particles
- Initial analyte content in substrate



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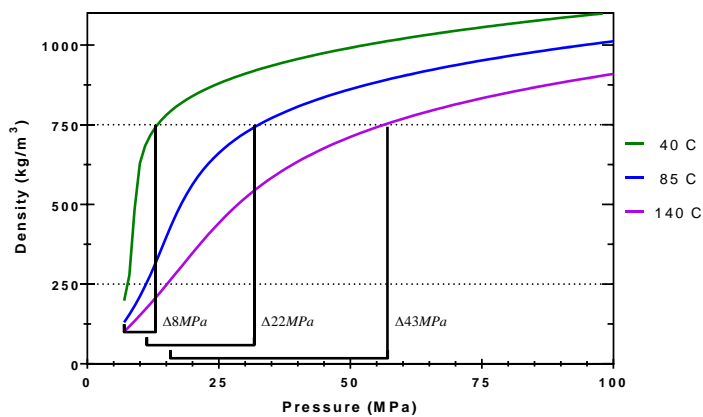
# Tuning Potential

CO<sub>2</sub> Isotherm

67

67

# Tuning "Green"

CO<sub>2</sub> Isotherm

68

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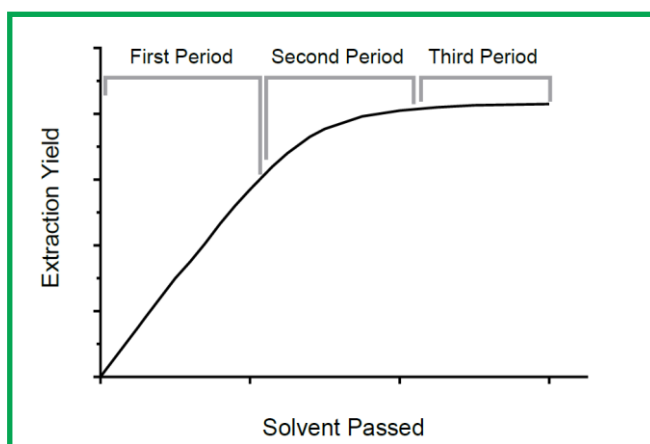
## Investigating inherency



69

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## Extraction Curves



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



70

70



## Experimental Setup

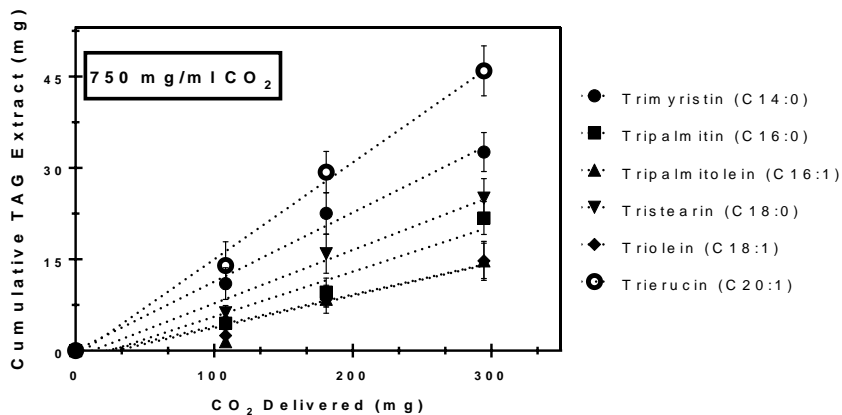
- Particle size
  - $<0.595\text{mm}$ ,  $>0.354\text{mm}$
- 25 mL vessel
- 200 mg
  - Analytical standards
  - *Scenedesmus dimorphus*
  - *Haematococcus pluvialis*
- 3-5 mg  $\text{CO}_2$  per minute



71

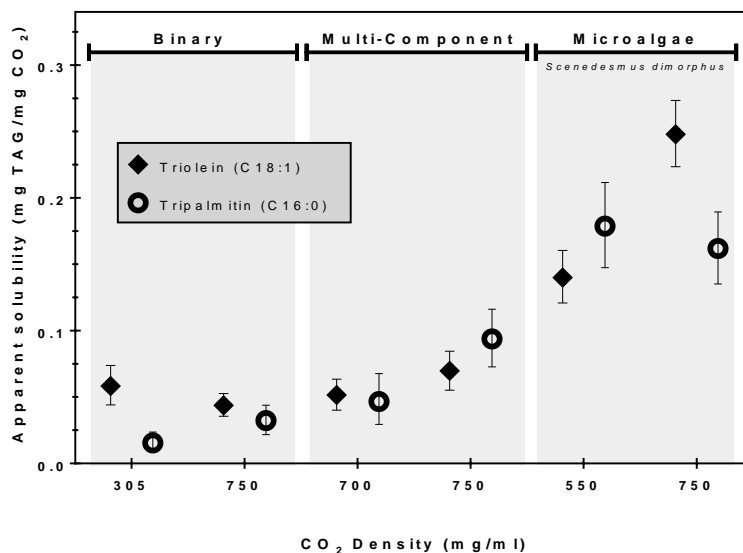
71

## Multi-Component



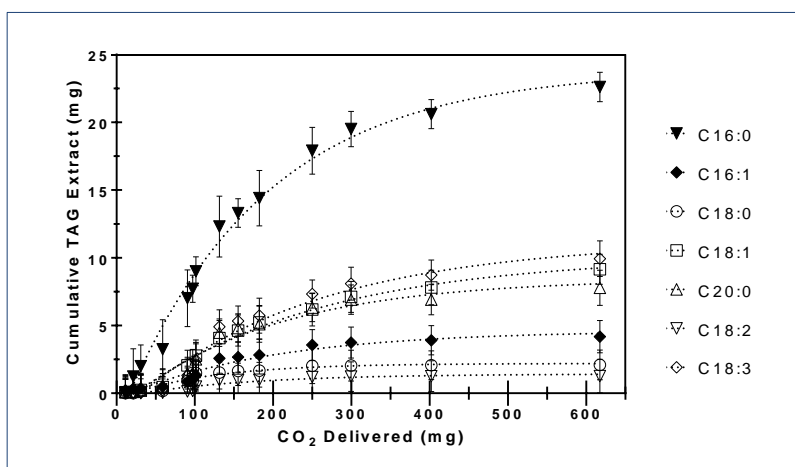
72

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73

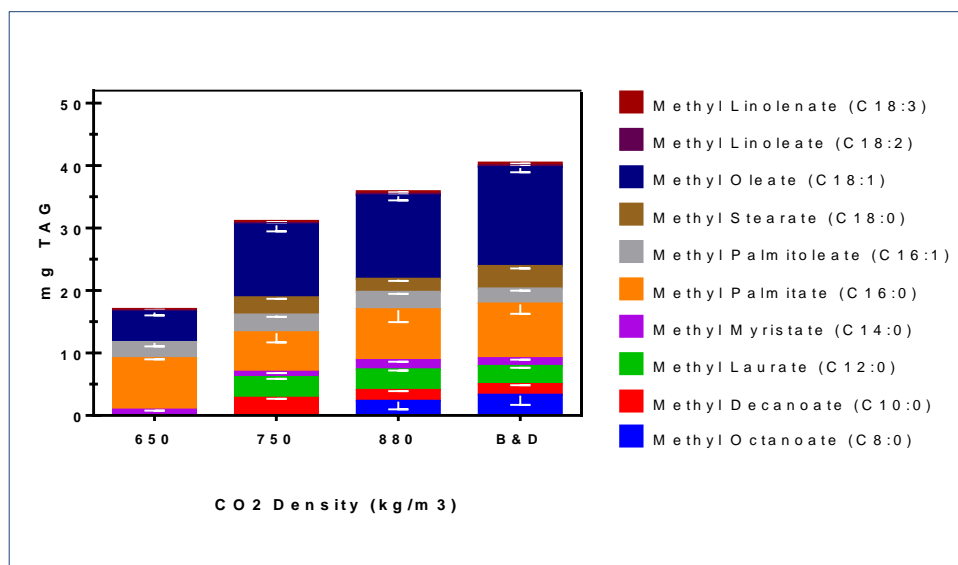
## Scenedesmus dimorphus



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## Enrichment



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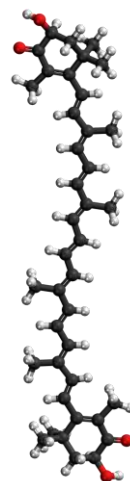
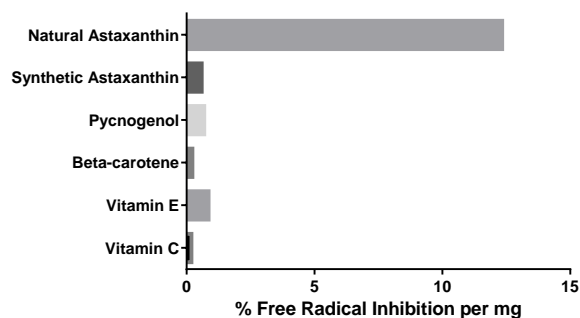


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## Red Antioxidant

- Carotenoids
  - Astaxanthin



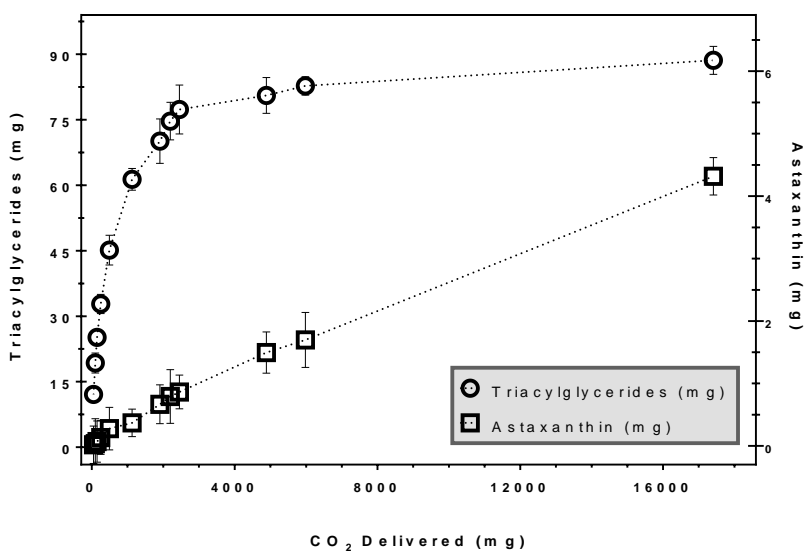
Capelli, B., et. al., *Synthetic astaxanthin is significantly inferior to algal-based astaxanthin as an antioxidant and may not be suitable as a human nutraceutical supplement*. *Nutraceuticals*, 2014, 12(4)

77



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## Haematococcus pluvialis



78



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# Dynamic Control

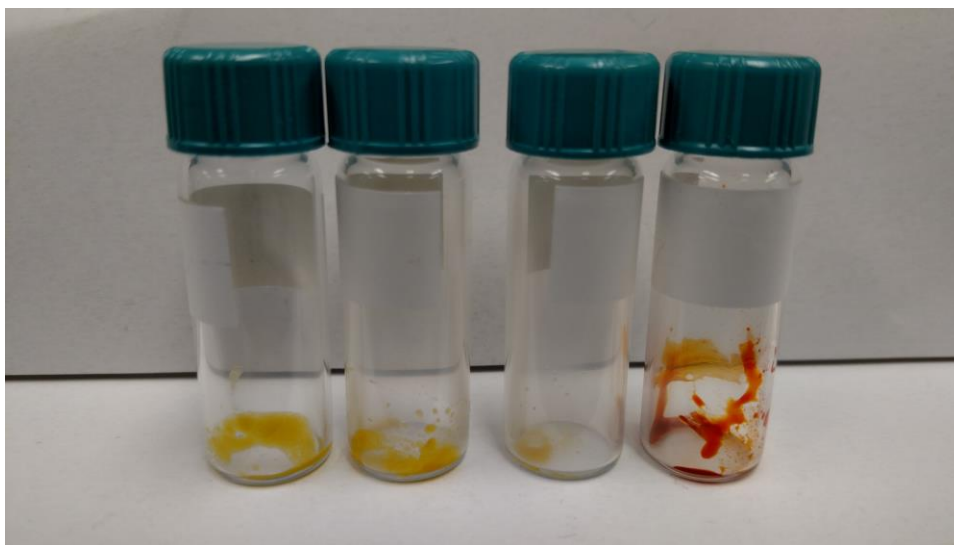
- Static control
  - Single density & polarity
  - Single operational parameters
    - Temperature
    - Pressure
    - Entrainer
- Dynamic control
  - Multiple densities & polarities



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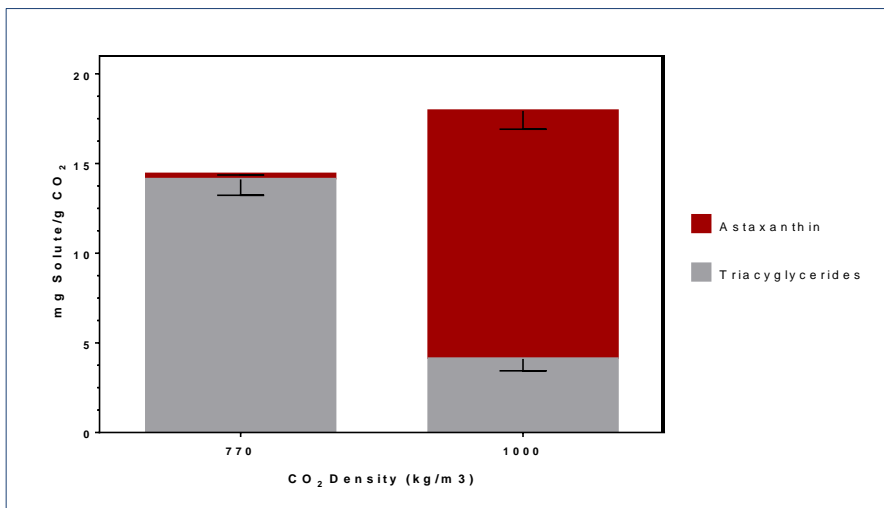
# Astaxanthin



80

80





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.

81

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## Back of the Envelope

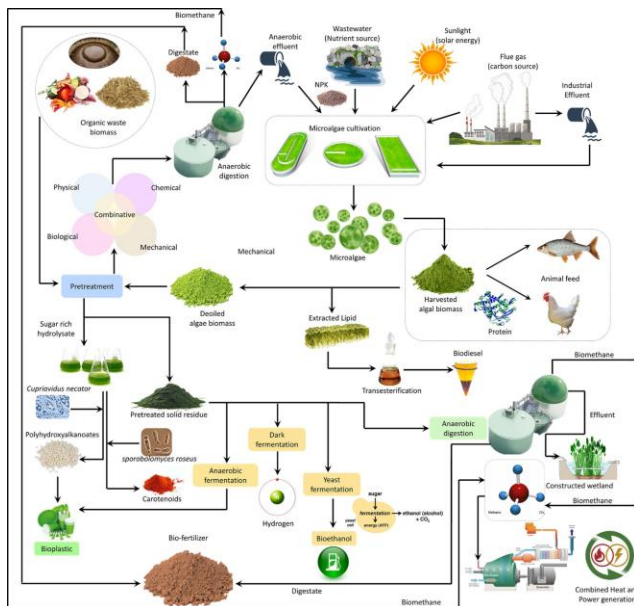
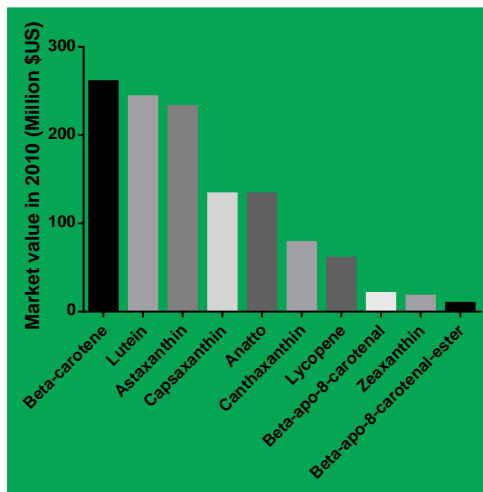
- Biodiesel → \$7/kg
- Astaxanthin → \$7000/kg
- CO<sub>2</sub> credits → ?/kg



82

82

# More value to find from an integrated biorefinery



Kannah RY, Kavitha S, Banu JR, Sivashanmugam P, Gunasekaran M, Kumar G. A mini review of biochemical conversion of algal biorefinery. *Energy & Fuels*. 2021 Oct 13;35(21):16995-7007.

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