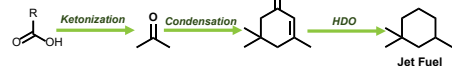
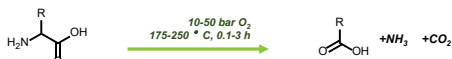


Background

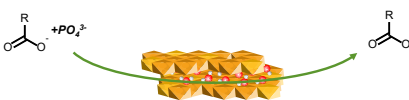
- Algae biomass consists of lipids, carbohydrates, protein, ash, and minor components.
- Pretreatment, fractionation and lipid extraction allow upgrading technology to be tailored to the chemistry of each fraction.
- Lipids and solubilized materials are readily upgraded to fuels and chemicals, but extracted solids are underutilized.

Component	Scenedesmus		
	IIRIND2	Extracted Solids	Extracted Liquor
Ash	8.7	29.3	9.4
Lipids	23.4	8.1	0.0
Protein	20.3	19.4	21.2
Carbohydrates	27.0	9.2	8.0
Acids	0.0	0.0	34.5
Other/unknown	20.6	33.9	26.9
Total	100.0	100.0	100.0

- Under some mild oxidizing conditions, amino acids are selectively deaminated and decarboxylated to carboxylic acids one carbon shorter than the amino acid.¹
- Under wet oxidation conditions, carbohydrates and other organic compounds are also oxidized to carboxylic acids.
- Carboxylic acids can be upgraded to high-performance fuels by ketonization, condensation, and hydrodeoxygenation.²

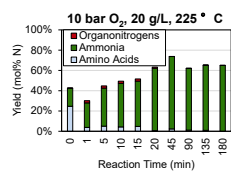
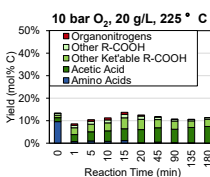


- If wet oxidation can funnel organics to fuel precursor carboxylic acids while releasing protein nitrogen as NH_3 , it would be a robust strategy for valorizing the extracted solids.
- Recovery of NH_3 via ion exchange in the presence of carboxylic acid anions is conceptually feasible, but selective recovery of anionic PO_4 may be more challenging due to competition with anionic carboxylic acids.
- Hypothesis: selective anion exchange materials, such as hydrotalcites,³ should allow selective recovery of PO_4 while leaving carboxylic acids in solution.**



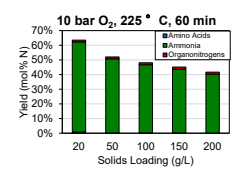
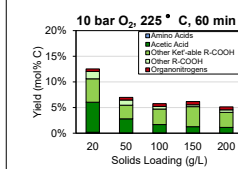
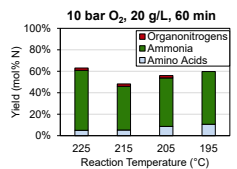
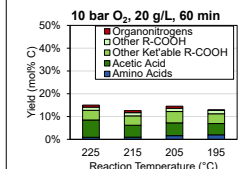
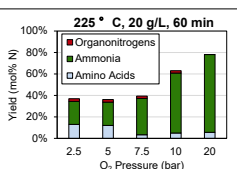
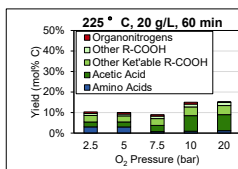
Results

- With Extracted Solids, carboxylic acid yields are < 15%, while N yields as NH_3 are > 40%
- Carboxylic acid yields do not improve after ~15 min reaction, while NH_3 yields continue to rise through ~45 min reaction time
- Carboxylic acid yields are also relatively insensitive to O_2 pressure, though amino acids are not fully converted at lower O_2 pressures. In contrast, NH_3 yields increase significantly as O_2 pressure increases
- Both yields are relatively insensitive to temperature, though amino acids are not fully converted at lower temperatures
- Both carboxylic acid and NH_3 yields decrease as solids loading increases
- Based on these results, we hypothesized that oxidation may be limited by solubilization of the substrate

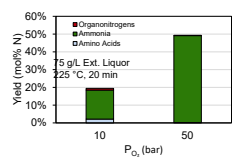
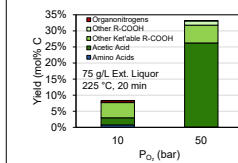


Valorization of algal biomass to fuels and chemicals frequently requires pretreatment to lyse cells and extraction to recover lipids, producing an aqueous lysate and an extracted solid residue as intermediates. Mild Oxidative Treatment (MOT) is a promising wet oxidation route to simultaneously convert nitrogen contained in the lysate and residues to easily-recyclable ammonia and to convert carbon in the same fractions to carboxylic acids that can be converted to biofuels by ketonization, condensation, and hydrodeoxygenation. We show that for a *Scenedesmus* algae under certain oxidation conditions, nearly all of the nitrogen in the residues can be converted to ammonia and recovered by cation exchange, while almost half of the carbon can be converted to carboxylic acids. At the same time, we also show that soluble phosphorus in the form of phosphate can be selectively recovered by anion exchange, leaving a clean aqueous carboxylic acid stream for upgrading to fuels.

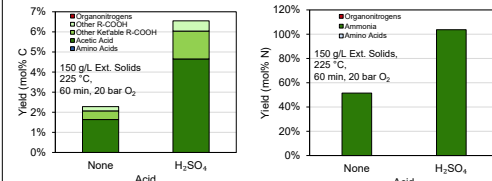
Mild Oxidative Treatment of algae residues facilitates N and P recycle by ion exchange and fuel production via carboxylic acid intermediates



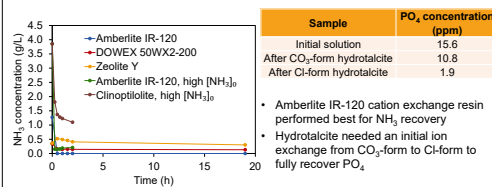
- Using the Extracted Liquor, both carboxylic acid and NH_3 yields increase significantly with O_2 pressure, which is not observed with the extracted solids, suggesting MOT of extracted solids is limited by feedstock solubilization rather than O_2 availability



Improvement and Integration



- Addition of 1 wt% H_2SO_4 during MOT to increase solubilization improves carboxylic acid yields 3x and allows quantitative recovery of nitrogen as NH_3 . Higher carboxylic acid yields are available at lower solids loadings.



Scenedesmus extracted liquor	Total N (g/L)	Protein N (g/L)	PO_4 N (g/L)	N recovery	P recovery	Carboxylic acids (g/L)	Carboxylic acid recovery
Before wet oxidation	1.22	0.56	0.39			4.27	
After wet oxidation	0.69	0.00	0.42	78.5%		4.17	97.7%
After cation exchange	ND	ND	0.12		72.5%	3.80	89.0%

- In authentic MOT solution, more than 75% of NH_3 and more than 70% of PO_4 were recovered by ion exchange (unoptimized).
- At the same time, nearly 90% of carboxylic acids remained in solution.
- An alternative approach, precipitation of PO_4 as Mg , Ca , and/or NH_4 salts was ineffective.

Conclusions

- Mild Oxidative Treatment may be limited by solubilization of the substrate.
- Ion exchange resins are more effective than zeolites for NH_3 uptake.
- Chloride-form hydrotalcite is selective and effective for PO_4 removal in the presence of carboxylic acids.
- Direct precipitation of PO_4 from MOT solutions was ineffective, possibly due to the presence of carboxylic acids.

Experimental

- MOT was conducted in 75 mL Parr reactors using 30 mL liquid volume. The desired amount of extracted solids, water, and/or extracted liquor were added to the reactor, the reactor was sealed and leak checked, and heated to the desired temperature. Heating typically took 30 minutes. The desired pressure of O_2 was added when the reactor reached the desired temperature. After the desired reaction time, reactors were quenched in cool water, which typically took 30 min.
- Reactor solutions were filtered through a 0.2 μm filter and analyzed by GC-MS after derivatization with propylchloroformate. The derivatization and analysis followed the procedure of Kaspar et al.,⁴ except that propylchloroformate was used instead of a chloroform solution, pyridine was used instead of picoline, diethyl ether was used instead of isooctane, and the GC column was a 30 m x 0.25 mm ID RTX-50. These modifications allow separation of derivatized formic and acetic acid from the solvent peaks. Phosphate was analyzed by ion chromatography.
- Cation exchange employed 1 g resin or zeolite and 4 mL solution, stirring at room temperature for the desired amount of time. Anion exchange employed 0.4 g hydrotalcite and 4 mL of solution, stirred for 2 h.

References
¹Stadlman, *Annu Rev Biochem*, 1993, 62:797-821
²Huo et al., *Green Chem*, 2019, 21:5813-5827
³Kruger et al., *ACS Catal*, 2016, 6:1316-1328
⁴Kaspar et al., *J Chromatogr B*, 2008, 870:222-232