Electronic Supplementary Material (ESI) for Green Chemistry

Energy-Efficient Extraction of Fuel and Chemical Feedstocks from Algae

(Supporting Information)

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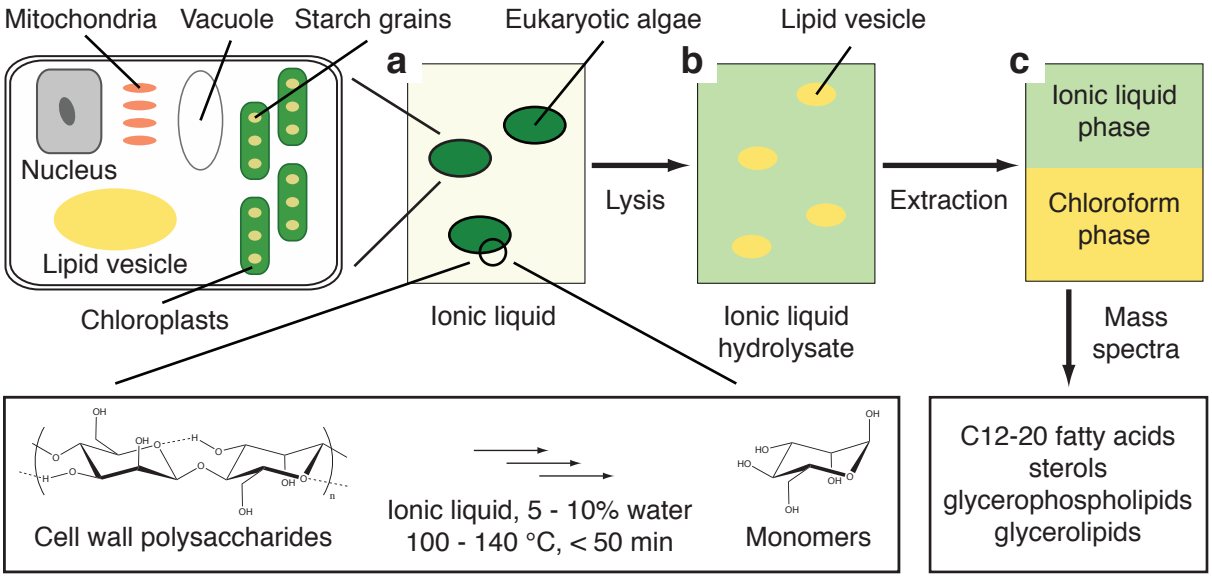
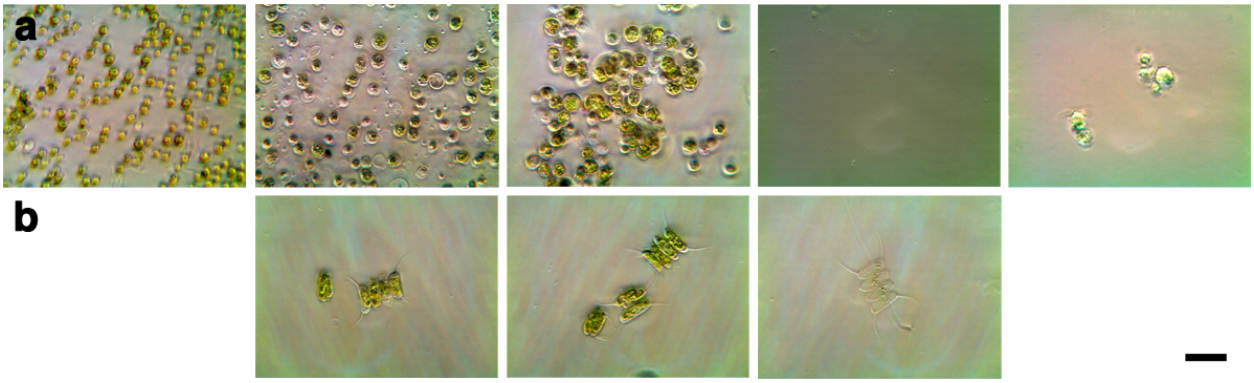
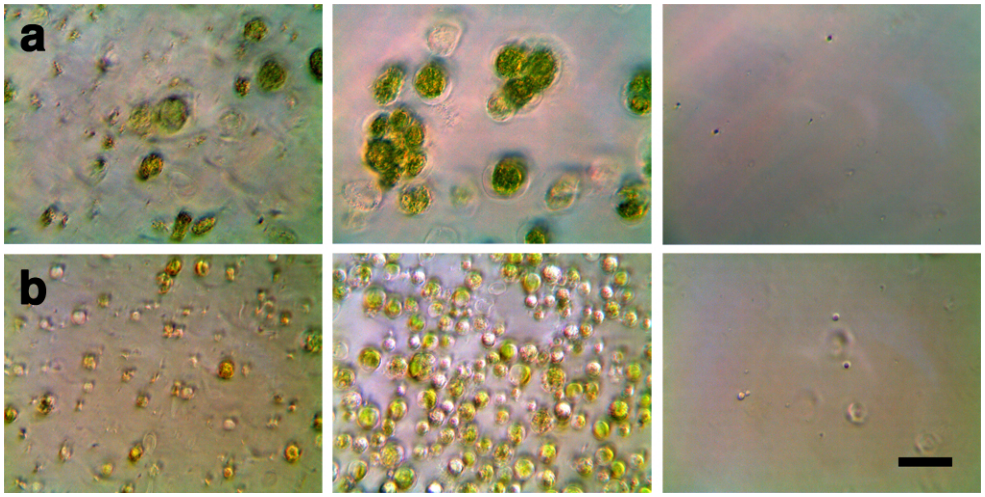
Supplementary Figures



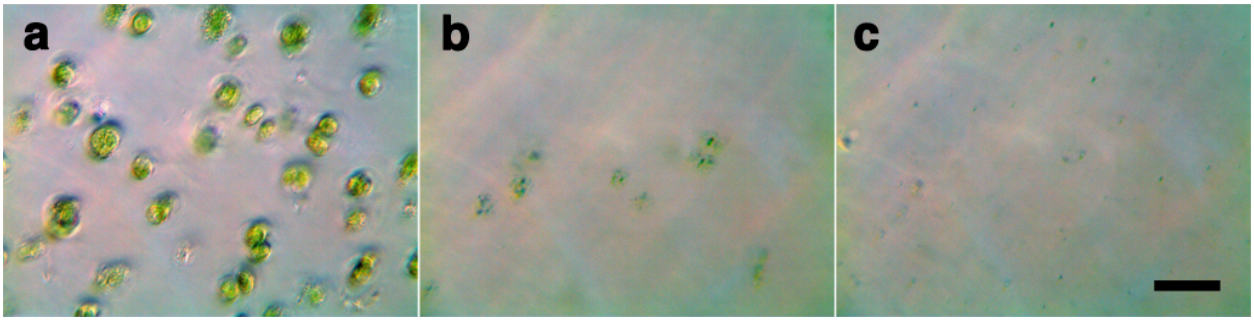
Supplementary Figure 1: Experimental schematic and summary of results. (**a**) Algae water suspensions initially mixed and dissolved in ionic liquids at temperatures of 100 to 140 °C and atmospheric pressure. The reaction scheme resulting in oligomerization of cell wall polysaccharides is shown. (**b**) Created cell-free mixture of algae in ionic liquid (hydrolysate). Some free-floating chloroplasts are seen and the background changes to light-green due to released chlorophyll. (**c**) Chloroform-extracted hydrolysate after centrifugation. The chloroform phase contained a wide range of lipids matching the profiles expected from algae.



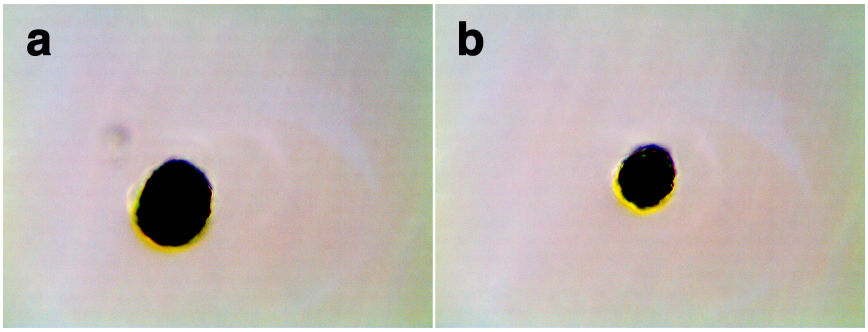
Supplementary Figure 2: Micrographs of *Chlorella pyrenoidosa* and *Scenedesmus quadricauda*. (a) *C. pyrenoidosa* and (**b**) *S. quadricauda* micrographs after (from left to right) 1 hour in boiling water, sonication for 30 min, direct sample of batch, reaction in [BMIM]Cl at 100 to 130 °C (run #7 and #13), reaction in [BMIM]Cl at 90 to 100 °C (run #4). Lower-right bar measures 10 µm.



Supplementary Figure 3: Micrographs of *Chlorococcum hypnosporum* and *Chlorella vulgaris*. (a) *C. hypnosporum* and (**b**) *C. vulgaris* micrographs after (from left to right) sonication for 30 min, direct sample of batch, reaction in [BMIM]Cl at 110 °C (run #12 and #9). Lower-right bar measures 10 µm.



Supplementary Figure 4: Micrographs of *Chlamydomonas moewusii* during lysis. (**a**) Direct sample of batch. (**b**) After 5 min in [BMIM]Cl at 120 °C, and (**c**) 10 min latter (run #10). Lower-right bar measures 10 µm.



Supplementary Figure 5: Hydrophobic ionic liquids. Ionic liquids formed by the cation 1-butyl-3-methylimidazolium paired with the anions (**a**) hexafluorophosphate and (**b**) bis(trifluoromethylsulfonyl)imide imparted hydrophobic characters. These ionic liquids did not dissolve or lyse algae (*Chlorella pyrenoidosa* shown). Instead, after evaporation of water, clustered cell masses were formed.

Supplementary Text

Cell wall toughness. The toughness of semi-crystalline cell wall microfibril networks giving structural support to algae cell walls was estimated from strain measurements by other researchers of bacterial cellulose sheets grown from *Gluconacetobacter xylinus* [1]. Both materials are of microbial origin and were assumed to be of roughly similar degree of polymerization, crystallinity and structure. Previous measurements of the engineering stress on a tensile test machine were inadequate due to difficulties in assessing the local strain and the effective cross-sectional area, which likely changed during deformation. Instead, stress-strain (σ-ε) curves were determined micromechanically, using a Raman spectrometer microscope to measure molecular deformation. By measuring the strain-calibrated displacement of the 1095 cm^{-1} band, a Young's modulus, *E*, of 41 GPa was determined for the network. Interestingly, assuming random fiber orientations, this value corresponds to a single fibril modulus of 114 GPa, similar to the stiffness of high-grade Kevlar® (124 GPa). Since the micromechanical stress-strain relationship was approximately linear, the toughness (*γ)* could be estimated as:

$$\gamma = \int_0^{\varepsilon_f} \sigma \, d\varepsilon \approx \frac{1}{2}\varepsilon_f^2 E = \frac{1}{2}(0.026)^2(41\times10^9) = 14 \text{ MPa}$$

or ~ 9 kJ/kg assuming a cellulose density of 1.5 Mg/m^3. For comparison, the toughness of graphite (carbon) fibers are ~ 12 kJ/kg ([2]).

Algae surface-to-mass ratio. From Northcote *et al.* [3] the radius of *Chlorella pyrenoidosa* is ~ 1.8 μm, which was adopted as a reasonable size for other algae. Assuming a spheroidal shape and a density of ~ 1 kg/m^3, the cell surface-to-volume and surface-to-mass ratios are:

$$S/V = 3/r = 2\times10^6 \text{ m}^{-1} \approx 10^6 \text{ m}^2/\text{kg}.$$

Note that the mass basis assumes a well-hydrated cell.

Energy balance calculation details. To facilitate calculation of the dissolution and hydrolysis enthalpies, cellulose was adopted as a representative polysaccharide. The dissolution enthalpy of cellulose in 1-butyl-3-methylimidazolium chloride at T = 373 K was calculated from:

$$\Delta h_i^m = \frac{RT \ln\left(x_i^L \gamma_i^L\right)}{\left(\frac{T}{T_i^m} - 1\right)}.$$

Here, Δh_i^m and T_i^m are the melting enthalpy and melting temperature of pure cellulose, respectively. However, the melting temperature is unknown, so the decomposition temperature (773 K) was adopted, giving an upper-bound estimate for the dissolution enthalpy. The mole fraction of dissolved cellulose at equilibrium with its solid form is x_i^L, which was measured experimentally to be 25% by weight [4]. The activity coefficient between cellulose and ionic liquid is γ_i^L. The value γ_i^L = 10^{-115} was obtained from calculations combining quantum mechanical computation of surface charge-density in a conductor, electrostatic interaction energy with a dielectric continuum and screening charge probability distributions [5]. This gives a dissolution enthalpy of < 24 kJ/kg. Assuming that cell wall polysaccharides constitute ~ 14% of dry biomass [3], dissolution consumes at most ~ 3 kJ/kg. The measured enthalpy change for the hydrolysis of cellulose oligomers in aqueous buffer was measured at ~ -4 kJ/kg of cellulose [6], or -560 J/kg of biomass.

It was assumed that an approach temperature of 5 K is feasible and no fouling occurs in the plate heat exchanger (counter-current geometry). The reactor and ionic liquid recycle were treated as adiabatic except for heat loss through the lipid output stream, calculated straightforwardly using the heat capacity of vegetable oil (1.67 kJ/kg-K). The separation of

solutes from ionic liquid and its recycle was assumed to consume 45% of the total process energy, following what is typically observed at chemical processing plants. The fraction of the total process energy supplied as work, or electricity, was taken to be the same as conventional algae extraction, or ~ 26% [7].

Supplementary Table 1: Energy balance for algae extraction process.

	Quantity	Unit	Basis	Reference
Lipid content	0.18		w/w	Lardon *et al.* (2009)
Carbohydrate content	0.50		w/w	Lardon *et al.* (2009)
Protein content	0.28		w/w	Lardon *et al.* (2009)
Cell wall content	0.14		w/w	Northcote *et al.* (1958)
Input cell concentration	0.10		w/w	
Heat ex. approach temperature	5	K		
Heat ex. heat loss	209	kJ/kg	Dry biomass	
Polysaccharide dissolution enthalpy	24	kJ/kg	Polysaccharide	
Polysaccharide hydrolysis enthalpy	-4	kJ/kg	Polysaccharide	Karim *et al.* (1989)
Heat loss via lipid stream	125	kJ/kg	Lipid	
Reactor net enthalpy change	33	kJ/kg	Dry biomass	
Separation contribution	0.45			
Total separation energy	198	kJ/kg	Dry biomass	
Total heat	0.3	MJ/kg	Dry biomass	
Total electricity	0.1	MJ/kg	Dry biomass	

Supplementary Table 1 Legend: The energy balance for the steady state process was calculated from contributions by the heat exchanger, reactor, and ionic liquid chromatography (separation) steps.

Well-to-Station net energy gain calculation details. The WTS model started from values calculated by Lardon *et al.* for all scenarios [7]. Please refer to the original article for a description of the assumptions. In the present work, all values were normalized to the basis of 1 kg of dry algae biomass. The energy requirements for wet extraction related to pressure homogenization. Here, both the values from Lardon, which were extrapolations form dry extractions, and actual reported cases of algae processing [8, 9] were taken into account to derive a range from 4 to 9 MJ/

kg. The partition of this total energy into heat and electricity followed the dry extraction case. Even though algae compositions varied significantly between normal and low N conditions, their impact on the ionic liquid based process energy was negligible. Material flows from the original study were beyond the present scope. Produced energy was estimated as extracted lipid plus oilcake (mostly sugars and proteins) assuming 100% energy extraction of all components.

Supplementary References

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