Lipid extraction of microalgae and hydrothermal carbonization of the residual algal biomass for sustainable hydrochar production

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1. Introduction and Objectives

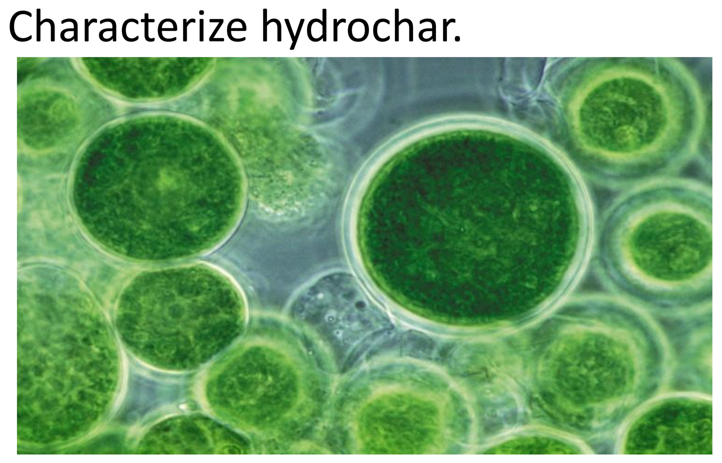
- To enhance the economics of algae technologies, value-added coproducts need to complement lipid production.
- Two routes for lipid extraction either "dried route" or "wet route". [1]
- For commercial development, cell disruption and lipid extraction from wet biomass need to be scalable and sustainable.
- The solid phase after lipid extraction is termed lipid extracted algae (LEA).
- Hydrothermal Carbonization (HTC) is a process where algal biomass is converted into a solid carbonaceous material called hydrochar. [2,3]

Table 1:Energy requirements for different steps in algal biodiesel production . [4]

Biodiesel production step (basis: 1kg of algal biodiesel)	Dry algal biomass (MJ)	Wet algal biomass (MJ)
Algae cultivation	7.5	10.6
Drying	90.3	0
Extraction	8.6	30.8
Oil transesterification	0.9	0.9
Total	107.3	42.3

Objectives of this study:

- Test cell disruption methods to identify the conditions for maximum lipid yield from *Nannochloropsis oculata*.
- Compare lipid yield among disruption methods.
- Extract lipids to obtain LEA.
- Apply HTC process to LEA in order to obtain hydrochar.
- Evaluate the hydrochar yield under various HTC experiments.
- Characterize hydrochar.



Hydrochar valorization: [5]

- Soil amendment
- Water treatment
- Solid fuel
- Capacitors
- Low cost adsorbents

2.Materials and experimental conditions

Materials:

- Algae species: Microalga *Nannochloropsis oculata* cultivated in outdoor novel horizontal bioreactor (HBR), harvested and washed with 0.9% salt water.
- A mixture of chloroform/methanol (2:1 % v/v) was used for the lipid extraction.
- LEA obtained after lipid extraction and oven dried to 15% moisture.

Methods & conditions:

- Cell disruption methods
- Hydrothermal sulfuric acid method [6]

Variables: a) Temperature: 105-125 °C, b) Residence time: 10-40 minutes and c) Acid concentration: 0.5-3%

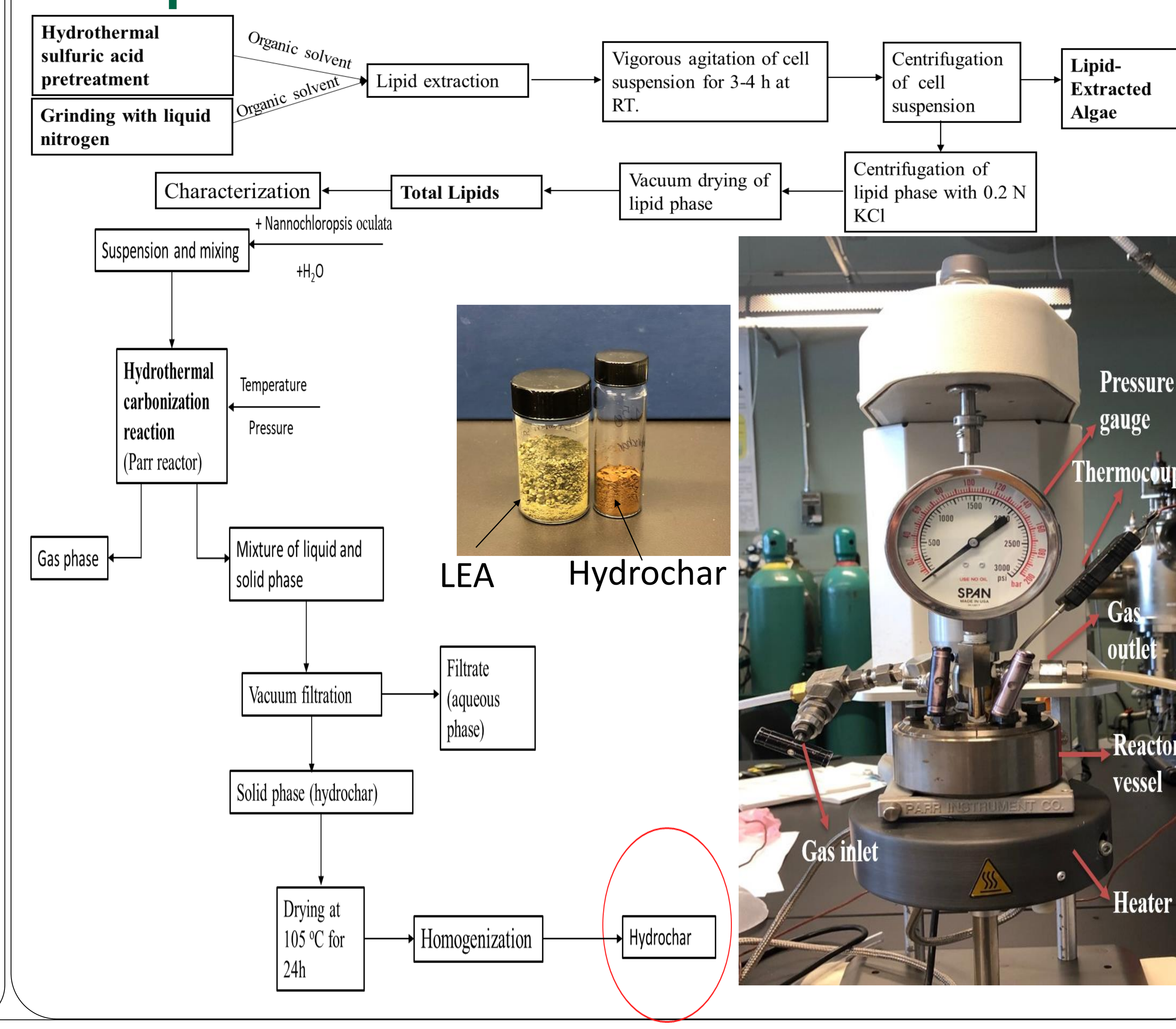
- Liquid nitrogen method [7]
- Mechanical method [1]
- Hydrothermal carbonization (HTC) [8]

Variables: a) Temperature: 175, 190, 205 & 220 °C, b) Residence time: 2h ,and c)Solid loading: 8 wt%

$$\text{Hydrochar Yield }\% = \left(\frac{Hydrochar\ mass}{LEA\ mass}\right) * 100\%$$

$$\text{Lipid yield}\% = \left(\frac{\text{Mass of extracted lipids}}{\text{Total mass of dried algae}}\right) * 100\%$$

3. Experimental Procedure

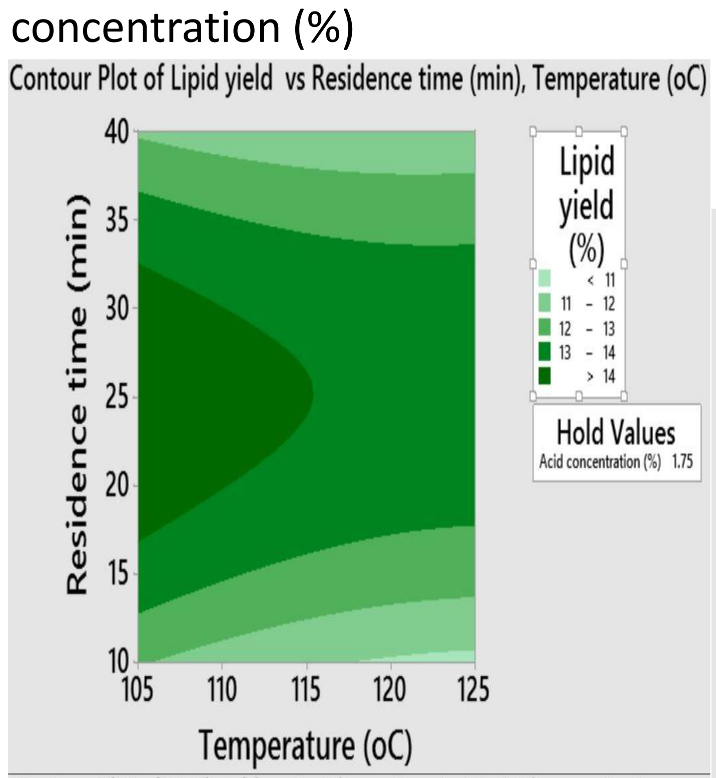


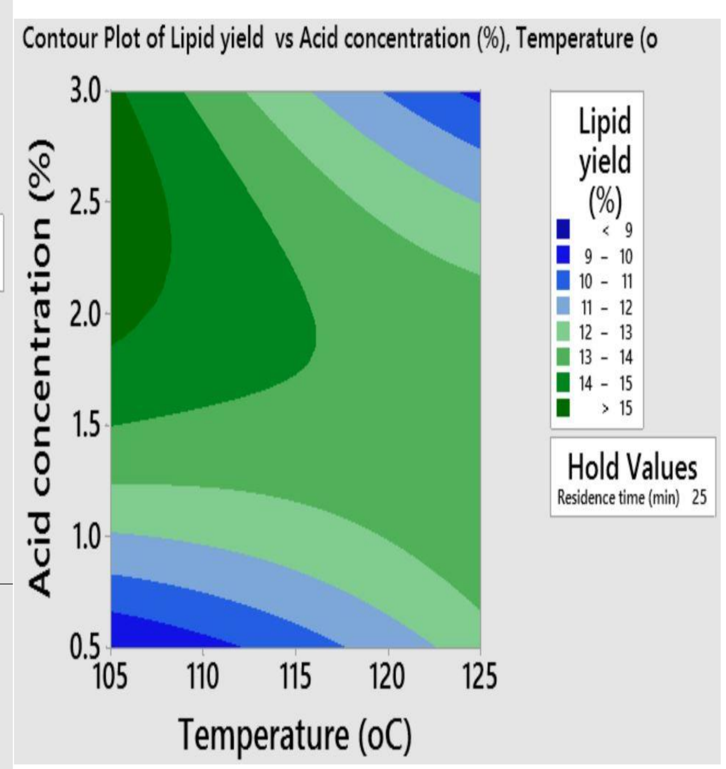
4. Results and Discussion

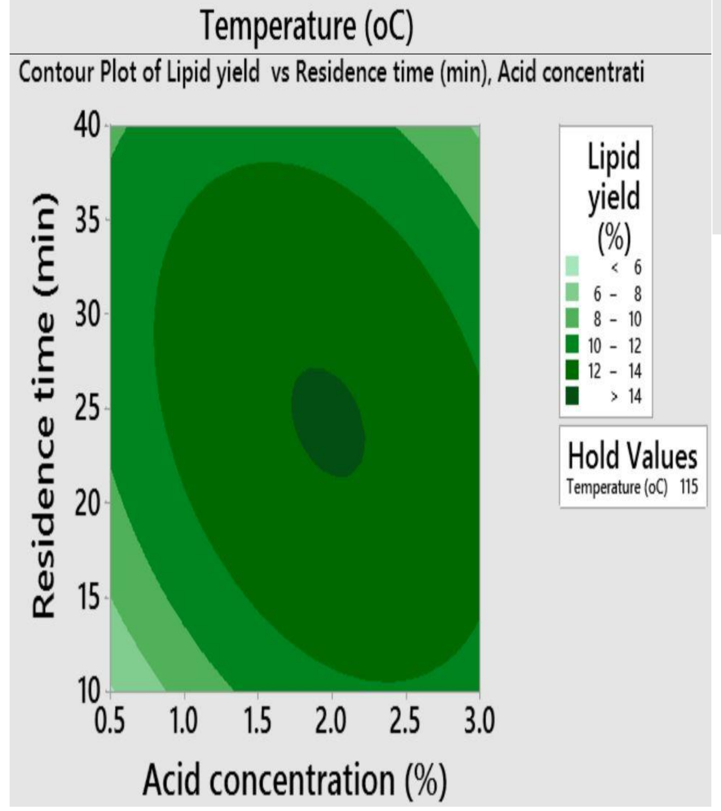
Sulfuric acid treatment statistical optimization

$$Y = 1 - 0.34 * X_1 + 0.655 * X_2 + 30.18 * X_3 + 0.00254 * X_1^2 - 0.01242 * X_2^2 - 1.707 * X_3^2 + 0.00124 * X_1 * X_2 - 0.1831 * X_1 * X_3 - 0.0984 * X_2 * X_3$$

Where: Y=lipid yield(%), X_1=Temperature, X_2= Time and X_3= Acid concentration (%)

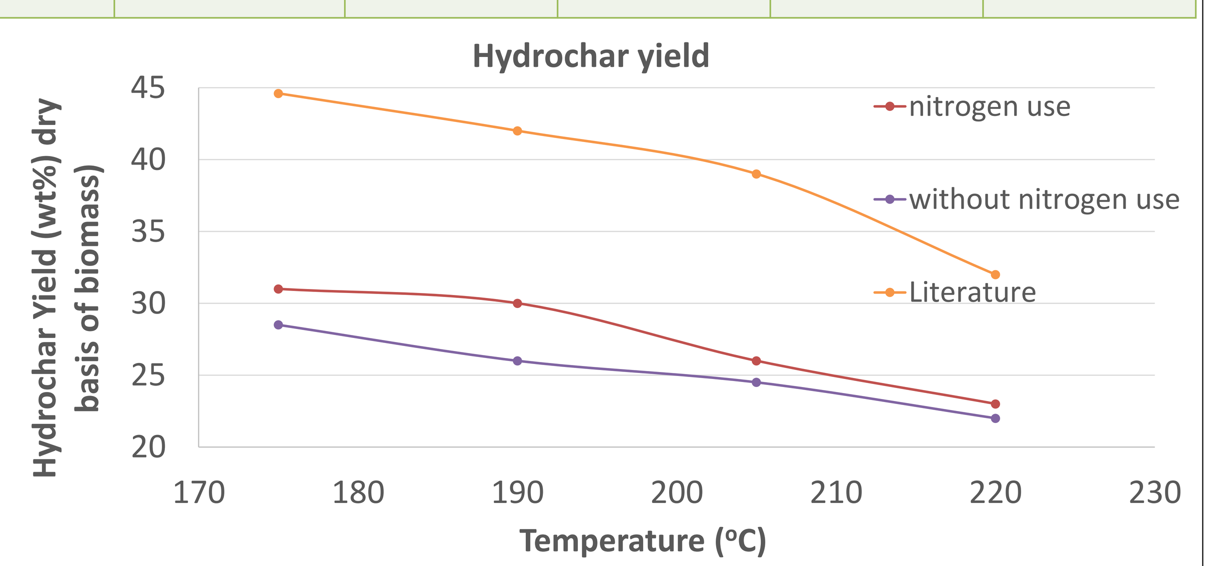


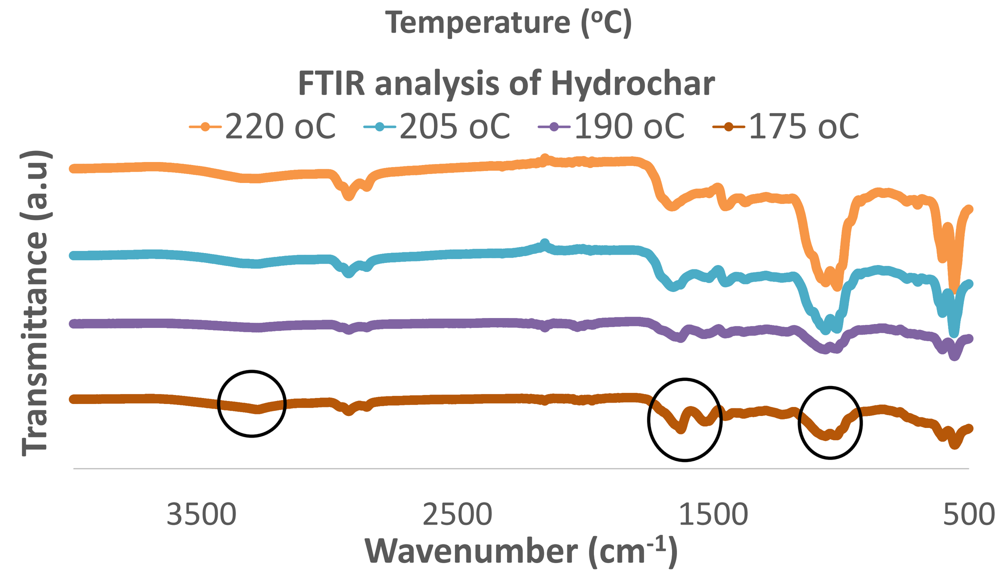




Hydrochar Yield, Surface Area, and Pore size

Temperature (°C)	*Hydrochar Yield % (Nitrogen Use)*	*Surface Area (m^2/g)*	*Pore Size (nm)*	*Hydrochar Yield % (without Nitrogen)*	*Hydrochar Yield % Literature [2,8]*
175	31	5.26	7.22	28.5	44.6
190	30	9.2	7.02	27	42
205	26	14.31	6.80	26	39
220	23	18.9	6.20	25.5	32





Cell disruption methods comparison

Method	Lipid yield (%)
Hydrothermal sulfuric acid	18.28
Liquid nitrogen	19.84
Mechanical	11.1

- The hydrochar yield was 23-31% and decreased as temperature increased.
- The surface area of hydrochar was 5.26-18.9 m^2/g.
- Functional groups :

1. O-H stretching vibration in hydroxyl and carbonyl groups
2. C=O stretching vibration of carbonyl group conjugated with aromatic ring
3. C=C stretching of the aromatic ring
4. Aromatic C-H bending vibration

Discussion:

- The maximum lipid yield with sulfuric acid treatment was 18.28% at 115 °C for 25 minutes with 1.75 % sulfuric acid concentration.
- Highest lipid yield was achieved with liquid nitrogen treatment.

5. Summary, Conclusions, and Future Prospects

- Sulfuric acid is a potential catalyst which leads to lipid extraction from N. oculata.
- The maximum lipid yield with sulfuric acid treatment is comparable with liquid nitrogen treatment.
- The maximum lipid yield was achieved around the central point based on the RSM model.
- HTC is a promising treatment to produce hydrochar from algal biomass.
- During HTC experiments, in the temperature range 175-220 °C, hydrochar was successfully produced.
- The autogenic pressure during the HTC experiments was 8- 25 bar depending on reaction temperature.
- The highest hydrochar yield was observed at lower temperatures. Hence, lower temperatures enhance the solid formation of the HTC reaction.
- The surface area of hydrochar increased at higher temperatures.
- The functional groups on the surfaces of hydrochars, which was determined by FTIR analysis, are in agreement with the ones reported in the literature. [2,3,8]

Future Prospects:

- Use a different lipid extraction mixture, which will be more environmentally friendly.
- Use a different treatment method with lower energy requirements.
- Investigate the influence of solids loading, residence time, and catalyst use on hydrochar yield and quality.
- Characterize the hydrochar and investigate potential applications.
- Optimize the experimental procedure in order to maximize hydrochar yield.

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