

Hydrothermal conversion of wastewater grown algal biomass into value added products and investigations on the effect of heavy metals on products

ABSTRACT

The present study has attempted to address the actual hurdles in the feasibility of algae-based fuels and products. An innovative algal biorefinery concept has been developed where algae is used for the remediation of municipal wastewater during its cultivation in a robust cultivation system, followed by its conversion to high value products in a sustainable manner. To start with, the first step of the study was to select microalgal species having potential of phycoremediation of metal contaminated water and biomass production in different forms of cultivation systems. For this, two different microalgal cultures; 1) *Chlorella pyrenoidosa* (CP) and 2) consortium of *Chlorella pyrenoidosa* and *Phormidium* (PA6) were cultivated in two different modes of cultivation systems i.e. in suspended and attached biofilm systems. The study aimed to highlight the suitability of an algal strain/consortium to different cultivation systems for metal removal and biomass production. The six commonly found heavy metals in wastewater; Cd, Cr, Pb, Cu, Ni and Zn, were used at 1 mg L⁻¹ of concentration. CP performed better in suspension systems with individual metal spiking. However, PA6 performed better in mixed metal spiked media (that was more close to the real wastewaters), especially in attached biofilm systems (>60% removal of all metals) and hence, it was selected for further studies. The next step was to produce the selected microalgae, PA6 in the attached cultivation systems using raw municipal wastewater at pilot scale (100 L) under outdoor natural conditions, followed by the valorisation of harvested algal biomass. The two biomass processing techniques investigated in the study were hydrothermal liquefaction (HTL) and anaerobic digestion (AD) to produce biocrude and biogas, respectively. For both the processing systems, Net Energy Ratios were calculated (from biomass cultivation to the biocrude/biogas production) and compared to find out which of the two energy conversion routes was energetically more favourable. The wastewater grown algae produced 346.59 ±5 mL g⁻¹ VS_{fed} of cumulative biomethane after AD, and 43±2% (dried biomass basis) of biocrude after HTL, respectively. NER_{HTL} (0.08) was observed to be higher than the NER_{AD} (0.007), proving HTL to be a comparatively better route in terms of energy recovery from the wastewater grown algal biomass.

Further, the Life Cycle Assessments (LCAs) was performed for 3 developed algal biofilms-based conversion systems; 1) wastewater grown algae (WWA) processed via anaerobic digestion (AD), 2) wastewater grown algae processed via hydrothermal liquefaction (HTL) and 3) synthetic media grown algae processed via HTL. Results showed that HTL of wastewater grown algae had 41.1 % lesser impact compared to AD of the same biomass and 98% lesser impact than HTL of synthetic media grown algae. The former process also showed positive impact on the eutrophication reduction due to the treatment of wastewater (59-92% nutrients removal) during cultivation. The global warming potential for biocrude production from WWA was 10 times lower than biomethane production from the same biomass and 21 times lower than the biocrude production from synthetic media grown algae. The results of the comparative LCAs proved that HTL of wastewater grown algae is a more sustainable route for valorizing the biomass than AD of wastewater grown algae or HTL of synthetic media grown algae.

The HTL of the biomass (water:biomass ratio of 4:1) at 27 bars (using N₂ as the reaction gas), 230° C for 20 minutes of reaction time produced a biocrude that was rich in specialty

chemicals. The HTL biocrude yield was appreciable but it comprised of high nitrogen and oxygen content (that decreased its fuel value) and hence, it required upgradation (deoxygenation and denitrogenation). Furthermore, the GC-MS analysis of the biocrude showed the presence of high value compounds that required enrichment. Efforts were made to improve the quality (upgradation/enrichment) of the HTL products by varying the catalyst (ZSM-5 or KOH)/solvent (methanol or butanol)/reaction gas (CO₂) during the HTL reactions, keeping all other HTL conditions same as that of the optimized reaction. The biocrude yield from ZSM-5 catalyzed HTL was 55% of that obtained by K₂CO₃ catalyzed HTL, but with reduced nitrogen (1.2% of TS) and oxygen (22.3% of TS) content that increased its HHV to 44.5 MJ Kg⁻¹ (1.6 times of K₂CO₃ catalyzed HTL biocrude). The biocrude obtained from HTL with alcoholic solvents comprised of 38% and 52% esters and that with CO₂ as the reaction gas had >65% hydrocarbons in it. On the other hand, the LCMS analysis of aqueous fraction showed the presence of highly valuable pharmaceuticals (minoxidil and ethosuximide), that were quantified to be 18.96 ± 0.24 mg kg⁻¹ and 41.07 ± 0.42 mg kg⁻¹, respectively. Additionally, this calcium and phosphorus rich aqueous fraction was hydrothermally mineralized to produce a carbonated hydroxyapatite (25.5%, dried biomass basis), a bone mineralizer (synthetic bone).

Disposal of metal contaminated biomass after bioremediation poses challenges due to non-availability of suitable techniques. Hence, HTL of algal biomass obtained from heavy metal remediation in attached biofilm systems was performed to investigate the effect of metals on HTL products and study their fate. The biocrude yield from HTL of metal laden biomass was comparable to the biocrude yield from HTL of biomass without metal contamination (30%, dried biomass basis). The heavy metal analysis of the solid and aqueous fraction showed that >70% of the metals had partitioned into the solid fraction whereas <1% were in the aqueous fraction. The aqueous fraction was also rich in nitrate and phosphate which could be reused for algal cultivation. Hence, hydrothermal liquefaction could be a very useful technique for valorization of metal contaminated biomass for a sustainable biorefinery.

Algal cultivation in wastewater and outdoor natural conditions followed by HTL of the harvested biomass to recover in parallel high value biocrude, solids and aqueous fraction, could be a potential biorefinery approach targeting multiple sectors.